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## PATENT ABSTRACTS OF JAPAN

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(54) MANUFACTURE OF SOLID POLYMER ELECTROLYTE BATTERY, SOLID POLYMER ELECTROLYTE BATTERY, AND NONAQUEOUS SOLUTION ELECTROLYTE FOR BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To enhance the extraction efficiency of a plasticizer and provide a battery with no adverse effect caused by the remaining extracting agent by using the specified silicone compound as an extracting agent of the plasticizer in the manufacture of a solid polymer electrolyte battery using a nonaqueous solution electrolyte by jointly using the plasticizer.



SOLUTION: A solid polymer electrolyte battery is manufactured in such a process that a polymer composition containing a plasticizer and a polymer compound is formed in layer, the plasticizer is extracted with at least one low molecular weight organic silicone compound selected from a chain organic silicone compound represented by formula I (R is the same or different, non- substituted or substituted monovalent organic group, m is an integer of 0-7.) and a cyclic organic silicone compound represented by formula II (R is the same meaning as R in formula I, n is an integer of 3-10.). A nonaqueous solution electrolyte is impregnated in the polymer compound layer from which the plasticizer is extracted to form a solid polymer electrolyte layer.



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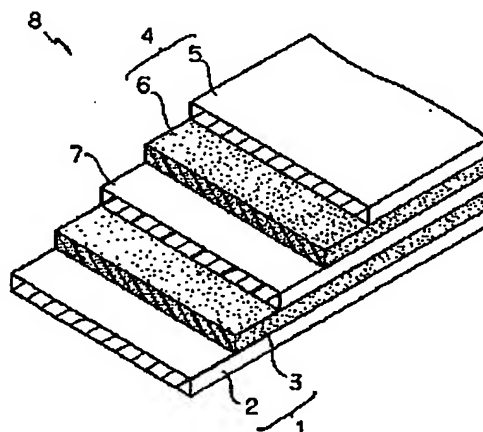
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(54) 【発明の名称】 固体高分子電解質型電池の製造方法、固体高分子電解質型電池および電池用非水溶液系電解液

(57) 【要約】

【課題】 非水溶液系電解液を用いた固体高分子電解質型電池を可塑剤を併用して製造するにあたり、可塑剤の抽出効率、非水溶液系電解液の含浸量等を高め、また抽出溶媒が残存しても電池系に影響を及ぼさないようにする。

【解決手段】 可塑剤と高分子化合物とを含有する高分子組成物を層状に成形した後、可塑剤を低分子量有機シリコン化合物を用いて溶解抽出する工程と、可塑剤が溶解抽出された高分子化合物層に非水溶液系電解液を含浸して、固体高分子電解質層を形成する工程とを適用して、水溶液系電解液を保持した高分子化合物層を有する固体高分子電解質層7を介して、正極1と負極4とが対向配置された固体高分子電解質型電池を製造する。





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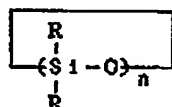
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【特許請求の範囲】

【請求項1】 非水溶液系電解液を保持した高分子化合物層を有する固体高分子電解質層を介して、正極と負極とが対向配置された固体高分子電解質型電池の製造方法において、

可塑剤と前記高分子化合物とを含有する高分子組成物を層状に成形した後、前記可塑剤を

【化1】



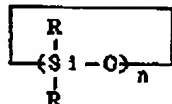
(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは3～10の整数を示す)

で表される環状有機シリコン化合物から選ばれる少なくとも1種の低分子量有機シリコン化合物を用いて溶解抽出する工程と、

前記可塑剤が溶解抽出された前記高分子化合物層に、前記非水溶液系電解液を含浸して、前記固体高分子電解質層を形成する工程とを有することを特徴とする固体高分子電解質型電池の製造方法。

【請求項2】 請求項1記載の固体高分子電解質型電池の製造方法において、前記正極および負極から選ばれる少なくとも1つの電極の活物質層を、前記非水溶液系電解液を保持する高分子化合物、活物質および可塑剤を含有する高分子組成物を層状に成形した後、前記可塑剤を前記低分子量有機シリコン化合物を用いて溶解抽出し、この可塑剤が溶解抽出された前記活物質を含む高分子化合物層に前記非水溶液系電解液を含浸して形成することを特徴とする固体高分子電解質型電池の製造方法。

【請求項3】 請求項1記載の固体高分子電解質型電池の製造方法において、前記非水溶液系電解液として、前記低分子量有機シリコン化合物を含む非水溶液系電解液組成物を用いることを特徴とする固体高分子電解質型電池の製造方法。

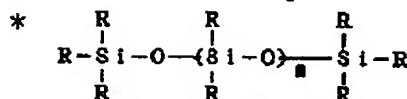


(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは3～10の整数を示す)

で表される環状有機シリコン化合物から選ばれる少なくとも1種の低分子量有機シリコン化合物を、イオン伝導性向上剤として含有する非水溶液系電解液組成物からなることを特徴とする固体高分子電解質型電池。

【請求項6】 請求項5記載の固体高分子電解質型電池において、

前記非水溶液系電解液組成物は、電解質、前記低分子量有機シリコン化合物、および溶媒和係数(SF値)が4.50



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは0～7の整数を示す)

で表される鎖状有機シリコン化合物、および

\* 【化2】

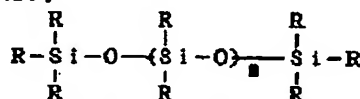
※電池の製造方法。

【請求項4】 請求項1記載の固体高分子電解質型電池の製造方法において、前記高分子化合物として、フッ化ビニリデンまたはフッ化ビニリデン-ヘキサフルオロプロピレン共重合体を用いることを特徴とする固体高分子電解質型電池の製造方法。

【請求項5】 非水溶液系電解液を保持した高分子化合物層を有する固体高分子電解質層と、前記固体高分子電解質層を介して対向配置された正極および負極とを具備する固体高分子電解質型電池において、

前記非水溶液系電解液は、

【化3】



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは0～7の整数を示す)

で表される鎖状有機シリコン化合物、および

【化4】

～13の炭化水素系溶媒を少なくとも含有することを特徴とする固体高分子電解質型電池。

【請求項7】 請求項5記載の固体高分子電解質型電池において、

前記高分子化合物層は、フッ化ビニリデンまたはフッ化ビニリデン-ヘキサフルオロプロピレン共重合体からなることを特徴とする固体高分子電解質型電池。

【請求項8】

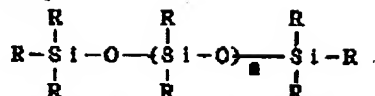




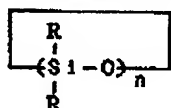
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【化5】



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは0~7の整数を示す)



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは3~10の整数を示す)

\*で表される鎖状有機シリコン化合物、および

【化6】

で表される環状有機シリコン化合物から選ばれる少なくとも1種の低分子量有機シリコン化合物を、イオン伝導性向上剤として含有する非水溶液系電解液組成物からなることを特徴とする電池用非水溶液系電解液。

【請求項9】 請求項8記載の電池用非水溶液系電解液において、

前記非水溶液系電解液組成物は、電解質、前記低分子量有機シリコン化合物、および溶媒和係数(SF値)が4~13の炭化水素系溶媒を少なくとも含有することを特徴とする電池用非水溶液系電解液。

【請求項10】 請求項8記載の電池用非水溶液系電解液において、

前記非水溶液系電解液組成物は、前記低分子量有機シリコン化合物を3~95重量%の範囲で含有することを特徴とする電池用非水溶液系電解液。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、非水溶液系電解液を用いた固体高分子電解質型電池の製造方法、固体高分子電解質型電池、および非水溶液系電池に用いられる電池用非水溶液系電解液に関する。

【0002】

【従来の技術】水分と激しく反応するために水を嫌うリチウム電池の電解液には、非水溶液系電解液を使用することが実用上の見地から不可欠であり、このようなリチウム二次電池が非水溶液系電池としてよく知られている。このようなリチウム二次電池は、電池エネルギー密度が大きいことから、小型軽量化を重視するコードレス機器の電源等として多用化されつつある。また、この電池機能を0.5mm程度の超薄型の単セルとして具備するリチウムイオン固体高分子電解質型二次電池(LPB)、すなわち非水溶液系電解液の保持機能を有する有機高分子化合物を固体電解質層として用いた電池の開発も活発に行われており、実用化レベルに達しつつある。これら二次電池の実用化には、正極並びに負極の活性物質の選択や電池構成法等、多くの要素技術の改良が寄与している

が、電解液の選択には一層の技術向上が望まれている。

【0003】ここで、水溶液系電池の電解液には、例えば水酸化カリウムの強アルカリ水溶液が用いられる。ここでの電池反応に対する電解液の作用効果は、水の低粘度でかつ比誘電率が大きいという液体特性、並びに水溶液としての水酸化カリウムによる約 $10^{-4} \Omega/\text{cm}$ 以上の良好なイオン伝導性によって、電池に必要な実用的な電池容量の発現および大きな負荷への対応を実現している。これに対して非水溶液系電池では、電池の使用電位差で安定で、かつ粘度の低い液体(溶媒)が少ないために、水溶液系電解液に比べると大きなイオン伝導性を維持することに苦慮しているのが現状である。特に、LPBタイプにおいては、使用する固体高分子電解質層中のイオン電解質含有量が50重量%以上程度にしないと、十分に実用性のある電池が得られないことが理論的にも実験的にも確認されている。

【0004】固体高分子電解質層中の電解質の含有量を高めるために、従来からいくつかの方法が試みられている。その技術の1つとして、アルキレンオキサイド等のヘテロ原子団を分子構造中に含む高分子化合物を固体高分子電解質層として用いる方法が挙げられる(特公平6-52671号公報参照)。このような固体高分子電解質層は、電解質を50重量%以上含浸させることが可能であることが知られている。しかし、固体高分子電解質層を構成する高分子構造の中で、電解質を含浸したヘテロ原子団が海相となり、ヘテロ原子団を除く高分子主鎖が島相を形成しているため、電解質を高含浸するほど島相の流動性が増すことになる。すなわち、電解質を高含浸するほど形状が不安定となることから、実用的な電池として長期使用に供するためには、電解質の含浸量を期待するほど多くすることができないのが現状である。

【0005】他の方法としては例えば米国特許第5,456,000号に記載されているように、結晶相と非晶質相とが混在した高分子化合物を固体高分子電解質層として用いて、この非晶質相に電解質を含浸する技術がある。この技術は前述のヘテロ原子団を有する固体高分子電解質



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層で見られるような形状保持の不安定性は実用上回避できるが、電解質の含浸率は高々30~40重量%程度であるため、イオン伝導率は $10^{-1} \sim 10^{-2} \Omega/\text{cm}$ 程度しか得られず、実用電池としては低く過ぎる。

【0006】このために、上記した米国特許第 5,456,000号には、高分子電解質となるフッ化ビニリデン-ヘキサフルオロプロピレン共重合体（以下、(VdF-HFP)共重合体と記す）のような高分子材料に、ジブチルフタレート、ジメチルフタレート、*trans*-ブトキシエチルホスフェートのような可塑剤を配合して、この可塑剤を配合した原料を用いて製膜し、この膜中から可塑剤をエタノールのような低級アルコール、ジエチルエーテル、テトラヒドロフラン、ヘキサンのような低沸点溶剤で抽出除去してから、電解質を含む非水溶液系電解液を含浸する技術が記載されている。このような方法を適用することによって、非水溶液系電解液の含浸率を60~70重量%とすることができ、イオン伝導率が $10^{-1} \sim 10^{-2} \Omega/\text{cm}$ に向上することが示されている。

【0007】上記した方法を採用する場合、可塑剤は電池の使用電位で酸化還元反応を起こすため、電池系では完全に除去しておく必要がある。しかし、上述したような従来の抽出溶媒は、可塑剤の溶解性や高分子化合物内部への拡散浸透性が不十分で、可塑剤の完全抽出に長時間要するというような問題や、また抽出溶媒が固体高分子電解質層中に残存した場合に、電池使用状態で酸化還元を受けて電池系に悪影響を及ぼすというような問題を有していた。さらに、上述した従来の抽出溶媒は、いずれも可塑剤を溶解抽出すると同時に固体高分子電解質層となる高分子化合物を収縮させ、非水溶液系電解液の含浸量を低下させてしまうという欠点を有していた。また、可塑剤の溶解抽出工程の作業環境等を考慮した場合、抽出溶媒は人体に対して安全であり、さらに最近注目されているように地球環境を阻害しない等の特性を有することが望まれる。

【0008】一方、非水溶液系電解液自体についても、充放電効率のより一層の向上等を目的とした改良が望まれている。すなわち、非水溶液系電解液は有機溶媒とそれに溶解されてその中でイオン移動を行うイオン性化合物（電解質）とから構成される。これらのうち、有機溶媒には高誘電率であることに加えて、電池の内部インピーダンスを高めないように、電池の作動温度においてイオン伝導を容易にする低粘性であることが求められる。従来の非水溶液系電解液の溶媒には、エチレンカーボネート等の高誘電率物質が使われているが、常温では固体であったり、また粘度の高い液体が多いために、実際の電解液は低粘度の溶媒と混合し、見掛けの電解液粘度を低くして金属イオンの移動度を損わないようにしている。また、低粘度の溶媒には、電極活物質層にリチウムイオン等の金属イオンをインターカレートあるいはデインターカレートしやすくするために、活物質の表面活性

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を向上させ得る液体であることが望まれる。

【0009】上述したような特性が要求される低粘度の溶媒としては、従来ジメチルカーボネート、ジエチルカーボネート等の鎖状カーボネート等が使用されているが、電池特性の向上を図る上で、非水溶液系電解液のより一層の低粘性化や電極活物質の表面活性を高めることが可能な溶媒が求められている。

【0010】

【発明が解決しようとする課題】上述したように、従来の可塑剤を併用した非水溶液系電池の固体高分子電解質層の製造工程においては、以下に示すような特性を有する可塑剤の抽出溶媒が求められている。すなわち、可塑剤との溶解性が大きく、かつ表面張力が小さくて固体高分子電解質層を構成する高分子化合物の内部まで速やかに拡散浸透する。可塑剤の抽出時に高分子化合物を収縮させることがない、抽出温度での蒸気圧が大きく速やかに揮散し、さらに万一高分子化合物層内に残存しても電池系に悪影響を及ぼさない、人体に安全であると共に地球環境を阻害しない、等の特性を有する可塑剤の抽出溶媒が望まれている。

【0011】また、非水溶液系電解液自体については、充放電効率の向上等を目的とした改良が望まれており、具体的には非水溶液系電解液をより一層低粘性化することができると共に、電極活物質の表面活性を高めることが可能な溶媒が求められている。

【0012】本発明は、このような課題に対処するためになされたもので、非水溶液系電解液を用いた固体高分子電解質型電池を可塑剤を併用して製造するにあたり、可塑剤の抽出効率や非水溶液系電解液の含浸率を高めると共に、万一抽出溶媒が固体高分子電解質層内に残存しても電池系に悪影響を及ぼすことがない固体高分子電解質型電池の製造方法および固体高分子電解質型電池を提供することを目的としており、さらにはより一層低粘性化や電極活物質の表面活性の向上を図った電池用非水溶液系電解液を提供することを目的としている。

【0013】

【課題を解決するための手段】上記目的を達成するために、種々の溶媒について検討を進めた結果、下記の(1)式で表される低分子鎖状有機シリコン化合物、および(2)式で表される低分子環状有機シリコン化合物は、(a)電池形成に用いる可塑剤の良溶液であり、ほとんどの可塑剤を容易に溶解して抽出除去する、(b)表面張力が15dyne/cm前後と従来の抽出溶液と比べても小さく、電池構成組成物の微細部分に迅速に浸透しやすい、(c)可塑剤の抽出時に高分子化合物を収縮させることがない、(d)抽出温度での蒸気圧が大きく速やかに揮散する、(e)人体に極めて安全であると共に地球環境を損うことがない等、固体高分子電解質層を可塑剤を併用して製造する際の可塑剤の抽出溶媒に求められる各種特性を有しており、それに加えて、(f)本質的に低粘度である



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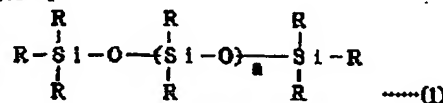
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と共に、電池使用状態の温度範囲における粘度変化が小さく、金属イオンの移動性を安定して高めることができる。(d)電池使用条件下で化学的な変化が少なく、電池系に影響を及ぼさないと共に耐酸化性に富む等、非水溶液系電解液の低粘度溶媒に求められる各種特性を有していることを見出した。

【0014】本発明は上記したような知見に基いて成されたもので、本発明の固体高分子電解質型電池の製造方法は、請求項1に記載したように、非水溶液系電解液を保持した高分子化合物層を有する固体高分子電解質層を介して、正極と負極とが対向配置された固体高分子電解質型電池の製造方法において、可塑剤と前記高分子化合物\*

\*物とを含有する高分子組成物を層状に成形した後、前記可塑剤を

【化7】

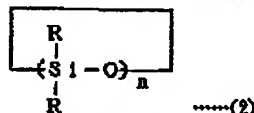


(式中、Rは同一または異なる非置換または

置換の1価の有機基を、nは0~7の整数を示す)

で表される鎖状有機シリコン化合物、および

【化8】



(式中、Rは同一または異なる非置換または

置換の1価の有機基を、nは3~10の整数を示す)

で表される環状有機シリコン化合物から選ばれる少なくとも1種の低分子置有機シリコン化合物を用いて溶解抽出する工程と、前記可塑剤が溶解抽出された前記高分子化合物層に、前記非水溶液系電解液を含浸して、前記固体高分子電解質層を形成する工程とを有することを特徴としている。

【0015】また、本発明の固体高分子電解質型電池は、非水溶液系電解液を保持した高分子化合物層を有する固体高分子電解質層と、前記固体高分子電解質層を介して対向配置された正極および負極とを具備する固体高分子電解質型電池において、前記非水溶液系電解液は、上記(1)式で表される鎖状有機シリコン化合物、および上記(2)式で表される環状有機シリコン化合物から選ばれる少なくとも1種の低分子置有機シリコン化合物を、イオン伝導性向上剤として含有する非水溶液系電解液組成物からなることを特徴としている。

【0016】さらに、本発明の電池用非水溶液系電解液は、上記(1)式で表される鎖状有機シリコン化合物、および上記(2)式で表される環状有機シリコン化合物から選ばれる少なくとも1種の低分子置有機シリコン化合物を、イオン伝導性向上剤として含有する非水溶液系電解液組成物からなることを特徴としている。

【0017】

【発明の実施の形態】以下、本発明を実施するための形態について説明する。

【0018】本発明の固体高分子電解質型電池の製造方法を非水溶液系のリチウム二次電池の製造方法に適用した一実施形態について説明する。製造方法について詳述する前に、まず非水溶液系リチウムの二次電池の構成について、図1を参照して説明する。なお、このリチウム二次電池は本発明の固体高分子電解質型電池の一実施形

態であり、本発明はこれに限定されるものではない。

【0019】図1は、この実施形態の固体高分子電解質型のリチウム二次電池の要部、すなわち電池セル部分を示しており、1は集電体2上に正極層3を積層形成して構成した正極である。また、4は集電体5上に負極層6を積層形成して構成した負極であり、この負極4の負極層6が正極1の正極層3と対向するように配置されている。これら正極1と負極4との間には、固体高分子電解質層7が正極層3および負極層6間に位置するように介在されている。これらによって電池セル8が構成されており、この電池セル8の巻回体や積層体等を電池容器に收容することによって、固体高分子電解質型のリチウム二次電池が構成される。

【0020】上記した正極1は、活物質、非水溶液系電解液およびこの電解液を保持する高分子化合物から構成される活性層としての正極層3を集電体2で担持した構造を有している。ここで、活物質としては種々の酸化物、例えばLiMnO<sub>2</sub>等のリチウムマンガン複合酸化物、LiNiO<sub>2</sub>等のリチウム含有ニッケル酸化物、LiCoO<sub>2</sub>等のリチウム含有コバルト酸化物、リチウム含有ニッケルコバルト酸化物、リチウムを含む非晶質五酸化バナジウム等や、例えば二硫化チタンや二硫化モリブデン等のカルゲコン化合物等を挙げることができる。なかでも、リチウムマンガン複合酸化物、リチウム含有コバルト酸化物およびリチウム含有ニッケル酸化物は、電界による劣化が少ない上に、電池として利用できる電荷の効率がよいことから好ましく用いられる。

【0021】上述した非水溶液系電解液は、有機溶媒等の非水系溶媒に電解質を溶解させることにより調整される。非水系溶媒としては、エチレンカーボネート(E

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ボネート (BC)、ジメチルカーボネート (DMC)、ジエチルカーボネート (DEC)、エチルメチルカーボネート (EMC)、 $\gamma$ -ブチロラクトン ( $\gamma$ -BL)、スルホラン、アセトニトリル、1,2-ジメトキシエタン、1,3-ジメトキシプロパン、ジメチルエーテル、テトラヒドロフラン (THF)、2-メチルテトラヒドロフラン等の一般的に電池用電解液として使用される有機溶媒に加えて、前述した (1)式または (2)式で表される低分子量有機シリコン化合物を挙げることができる。

【0022】通常、非水系溶媒は高誘電率を有する溶媒と低粘度の溶媒とを組合せた混合溶媒として使用され、低分子量有機シリコン化合物は低粘性溶媒の一種等として用いることができる。なお、この低粘性溶媒の一種等として用いられる低分子量有機シリコン化合物、およびこれを用いた非水系電解液組成物については後に詳述する。

【0023】また、上記した電解質としては、例えば過塩素酸リチウム ( $\text{LiClO}_4$ )、六フッ化リン酸リチウム ( $\text{LiPF}_6$ )、ヘキサフルオロリン酸リチウム ( $\text{LiBF}_4$ )、六フッ化砒素リチウム ( $\text{LiAsF}_6$ )、トリフルオロメタンスルホン酸リチウム ( $\text{LiCF}_3\text{SO}_3$ )、ビス(トリフルオロメチル)スルホニウムイミドリチウム [ $\text{Li}^+\text{N}(\text{CF}_3\text{SO}_2)_2$ ] 等のリチウム塩が挙げられる。これら電解質の非水系溶媒に対する溶解量は  $0.2 \sim 2\text{mol/l}$  程度とすることが好ましい。

【0024】上述したような非水系電解液を保持する高分子化合物としては、フッ化ビニリデン、フッ化ビニリデン-ヘキサフルオロプロピレン共重合体 ( $\text{VdF-HFP}$ ) 共重合体等のフッ素系高分子化合物、ポリエチレンオキシドのようなアルキレンオキシド系高分子化合物等を挙げることができる。この場合、ポリビニリデンフロライドやポリテトラフルオロエチレンのようなフッ素系高分子化合物を活性物質のバインダとして単独で用いたり、また ( $\text{VdF-HFP}$ ) 共重合体と混合して用いることを妨げるものではない。

【0025】上記した高分子化合物のうち、活性層としての正極層3を後述する固体高分子電解質層7と同様な方法で作製する場合には、フッ化ビニリデンや ( $\text{VdF-HFP}$ ) 共重合体を用いることが好ましい。なお、正極層3に導電性を与えるために、例えば人造黒鉛、アセチレンブラック等のカーボンブラック、ニッケル粉末等を併用することができる。

【0026】また、正極1の集電体2としては、例えばアルミニウムやニッケルの箔、メッシュ、エキスパンドメタル、パンチドメタル等が使用される。

【0027】負極4は、活性物質、非水系電解液およびこの電解液を保持する高分子化合物等から構成された活性物質層としての負極層6を、集電体5で担持した構造を有しており、負極層6が正極1の正極層3と対向するように、固体高分子電解質層7を介して配置されてい

る。負極4の基本構造および使用材料の一部は、上述した正極1と類似しているが、正極1と異なる材料はリチウムイオンをインターカレートする活性物質および集電体5の材質である。

【0028】すなわち、負極層6の構成要素の一つである活性物質には、リチウムイオンを吸蔵・放出する、すなわちインターカレートおよびデインターカレートすることが可能な、例えば炭素質材料が用いられる。この炭素質材料としては、例えばフェノール樹脂、ポリアクリロニトリル、セルロース等の有機高分子化合物を焼成して得られるもの、コークスやピッチを焼成して得られるもの、人造グラファイトや天然グラファイト等に代表される炭素質材料等を挙げることができる。なかでも、アルゴンや窒素等の不活性ガス雰囲気中にて、常圧または減圧下で  $773 \sim 3273\text{K}$  の温度で上記有機高分子化合物を焼成して得られるメゾカーボン、リチウムイオンのインターカレート特性に優れていることが知られている。もちろん導電性の向上を図るために、ケッチェンブラックやカーボンブラック等を併用してもよい。

【0029】また、負極4の集電体5としては、正極1でのアルミニウム等に代えて銅等を用いて、正極集電体2の外観形状と同様な形状のものを使用する。なお、負極層6の構成要素の一つである高分子化合物には、正極層3と同様なものが使用される。また、非水系電解液については上述した通りである。

【0030】上述した正極1と負極4との間に配置される固体高分子電解質層7は、上述したような非水系電解液およびこの電解液を保持する高分子化合物から構成される。すなわち、非水系電解液の保持機能を有する高分子化合物層に、非水系電解液を含浸して保持させることによって、固体高分子電解質層7が構成される。本発明においては、後に詳述するように、高分子化合物層を形成する際に可塑剤を併用し、この可塑剤を前述した (1)式または (2)式で表される低分子量有機シリコン化合物で抽出除去することによって、高分子化合物層に非水系電解液を高含浸させるものである。

【0031】固体高分子電解質層7の主体となる高分子化合物としては、フッ化ビニリデンや ( $\text{VdF-HFP}$ ) 共重合体等のフッ素系高分子化合物が用いられ、特に上述した非水系電解液の保持機能に優れる ( $\text{VdF-HFP}$ ) 共重合体が好ましく用いられる。この ( $\text{VdF-HFP}$ ) 共重合体において、フッ化ビニリデンは特に共重合体の骨格部で機械的強度の向上に寄与し、ヘキサフルオロプロピレンは共重合体に非晶質の状態で取り込まれ、非水系電解液の保持とリチウムイオンの透過部として機能する。このような高分子化合物からなる固体高分子電解質層7の基材層に含浸する非水系電解液については前述した通りである。

【0032】次に、上述した固体高分子電解質型リチウム二次電池の製造方法について説明する。





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【0033】まず、本発明の特徴の一つである固体高分子電解質層7の作製方法について述べる。すなわち、上述したフッ化ビニリデンや(VdF-HFP)共重合体等のフッ素系高分子化合物に可塑剤(可塑性溶媒)を配合して、高分子化合物層の形成材料となる高分子組成物を調製する。

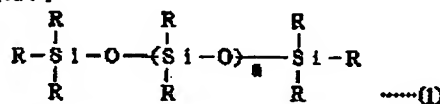
【0034】ここで、上記した可塑剤としては、ジブチルフタレート(DBP)、ジメチルフタレート(DMP)、ジエチルフタレート(DEP)、プロピレンカーボネート(PC)、*trans*-ブトキシエチルホスフェート 10 等が用いられる。また、これら可塑剤の配合量は、上記高分子組成物において20~70重量%の範囲とすることが好ましい。可塑剤の配合量が20重量%未満であると、非水溶液系電解液の保持量が不足して十分なイオン伝導性が得られないおそれがあり、一方可塑剤の配合量が70重量%を超えると、固体高分子電解質層7の基材層となる高分子化合物層の形状保持能や強度等が低下する。特に、本発明においては後述するように、可塑剤の溶解抽出効率が高い低分子量有機シリコン化合物を用いることから、可塑剤の配合量を50~70重量%の範囲と多量にしても、可塑剤残渣の発生を有効に防止することができる。すなわち、高分子化合物層に非水溶液系電解液を高\*

\*含浸させることができる。

【0035】上記したような高分子化合物と可塑剤とを含有する高分子組成物を有機溶媒に溶解させてペースト化し、この高分子組成物ペーストを層状に成形する。具体的には、高分子組成物ペーストを例えばナイフコーターで製膜した後、有機溶媒を揮散させて高分子組成物の層状成形体を作製する。この層状成形体は単独で形成してもよいし、また正極1や負極4との積層体として作製してもよい。

【0036】次に、上記した高分子組成物の層状成形体に含まれる可塑剤を溶解抽出する。この可塑剤の溶解抽出には、

【化9】

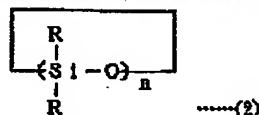


(式中、Rは同一または相異なる非置換または

置換の1価の有機基を、nは0~7の整数を示す)

20 で表される鎖状有機シリコン化合物、および

【化10】



(式中、Rは同一または相異なる非置換または

置換の1価の有機基を、nは3~10の整数を示す)

で表される環状有機シリコン化合物から選ばれる少なくとも1種の液状の低分子量有機シリコン化合物を用いる。

【0037】上記(1)式および(2)式におけるR基としては、メチル基、エチル基、プロピル基、ブチル基、オクチル基等のアルキル基、フェニル基、トリル基等のアリール基、ビニル基、アリル基等のアルケニル基、β-フェニルエチル基、γ-フェニルプロピル基等のアラールキル基等の非置換の1価の有機基、およびこれらの基の炭素原子に結合した水素原子をハロゲン原子、シアノ基、水酸基、カルボキシル基、カルボニル基、アミノ基、アルコキシ基等で置換した1価の有機基が例示される。中でも、安定性等の点からメチル基やフェニル基が好ましく用いられ、特に揮発性等の点からメチル基が望ましい。

【0038】また、上述した(1)式におけるmは0~7の整数であり、(2)式におけるnは3~10の整数である。mおよびnが上記した範囲を超えると、粘度、揮発性、安定性等が低下する。特にmおよびnは低粘度および良好な安定性等が得る上で、mは0~5の範囲とすることが、またnは3~7の範囲とすることが望ましい。

30 上記した低分子量有機シリコン化合物の具体例としては、ヘキサメチルジシロキサン(MM)、オクタメチルトリシロキサン(MDM)、デカメチルトetraシロキサン(MD2M)等の鎖状ポリメチルシロキサンや、オクタメチルシクロテトラシロキサン(D4)、デカメチルシクロペンタシロキサン(D5)等の環状ポリメチルシロキサン、さらにはこれらのメチル基の一部もしくは全てを他のアルキル基、フェニル基、アラールキル基、アルコキシ基、エステル基、アミノ基、エポキシ基、ハロゲン置換基等で変性した化合物等が挙げられる。

40 【0039】上述したような低分子量有機シリコン化合物による可塑剤の抽出は、可塑剤を含む高分子組成物の層状成形体を低分子量有機シリコン化合物(液体)に浸漬したり、あるいは低分子量有機シリコン化合物の蒸気浴に可塑剤を含む高分子組成物の層状成形体を晒す等の種々の方法により実施することができる。また、低分子量有機シリコン化合物に浸漬する際には、加温、振動、超音波照射等を併用することもできる。

【0040】ここで、上述したような可塑剤の抽出溶媒には、種々の可塑剤を良好に溶解し得ること、高分子組成物の層状成形体の内部深くにまで速やかに浸透して効



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率よく可塑剤を溶解し得ること、可塑剤の溶解抽出後には速やかに揮散して残存しないこと等が求められる。なお、可塑剤の溶解抽出後における速やかな揮散は、従来の可塑剤抽出溶媒は残存すると電池電圧で酸化還元を受け、電池特性に悪影響を及ぼすために求められていた特性である。

【0041】このような可塑剤抽出溶媒への要求特性に対して、上述した低分子量有機シリコン化合物の物性上の共通する特徴は、まず第1に上記したような可塑剤の良溶液であり、従ってほとんどの可塑剤を容易に溶解して、これを効率よく抽出除去することができる。

【0042】第2に、表面張力が15dyn/cm前後と従来の抽出溶媒と比べても小さく、高分子組成物の層状成形体の内部や微細部分等に迅速に浸透して、可塑剤を短時間で抽出除去することができる。特に、固体高分子電解質層7を正極1や負極4との積層体として処理、作製する際には、低分子量有機シリコン化合物の良好な浸透性がより一層効果を発揮する。

【0043】第3に、揮散性に優れることから、可塑剤の溶解抽出後には速やかに揮散し、可塑剤の抽出工程を効率よく実施することができる。ただし、後に詳述するように、上述した低分子量有機シリコン化合物は、固体高分子電解質層7中に残存しても電池特性に悪影響を及ぼすおそれがなく、また単に悪影響を及ぼさないだけでなく、非水溶液系電解液の低粘性化、すなわちイオン伝導度の向上に寄与するため、電池特性の向上を図ることができる。

【0044】さらに、上記したような特徴に加えて、上述した低分子量有機シリコン化合物は高分子組成物の層状成形体から可塑剤を溶解抽出する際に、固体高分子電解質層7の基材となる高分子化合物をほとんど収縮させることがない。これによって、より多くの非水溶液系電解液を含浸することが可能となる。これはイオン伝導度の改善に寄与する。また、上述した低分子量有機シリコン化合物は人体や環境等に対して極めて安全であるため、電池の製造作業環境並びに地球環境を損うことがない等という利点も有している。

【0045】上述したように、高分子組成物の層状成形体からの可塑剤の溶解抽出に、(1)式または(2)式で表される低分子量有機シリコン化合物を用いることによって、可塑剤を残存させることなく短時間で効率よく可塑剤を抽出除去することが可能となる。また、溶解抽出に用いた低分子量有機シリコン化合物は短時間で揮散し、たとえ低分子量有機シリコン化合物が残存したとしても、電池特性に悪影響を及ぼすことはない。さらには、高分子化合物をほとんど収縮させることがないため、より多くの非水溶液系電解液を含浸させることが可能となる。

【0046】低分子量有機シリコン化合物で可塑剤を溶解抽出した高分子化合物層が固体高分子電解質層7の

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基材層となる。そして、この高分子化合物層に非水溶液系電解液を含浸させることによって、固体高分子電解質層7が得られる。高分子化合物層に対する非水溶液系電解液の含浸量は、前述したように20〜70重量%の範囲、特に50〜70重量%の範囲とすることが好ましい。

【0047】次に、正極1および負極4の作製方法について述べる。正極1の作製にあたっては、まず前述した活物質、非水溶液系電解液を保持する高分子化合物、および必要に応じて導電性材料を、上記高分子化合物が可溶な有機溶媒に混合してペーストを調整する。次いで、このペーストを製膜することにより電解液未含浸の正極層3を得る。これを集電体1に積層し、これに非水溶液系電解液を含浸させることによって正極1が得られる。あるいは、上記ペーストを集電体2に塗布し、これに非水溶液系電解液を含浸させることができる。非水溶液系電解液の含浸は、固体高分子電解質層7との積層体を作製した後に実施してもよい。なお、負極4も基本的には正極1と同様に作製される。

【0048】ここで、活物質層である正極層3および負極層6は、前述した固体高分子電解質層7と同様に、可塑剤を配合した高分子組成物を用いると共に、可塑剤を上述した低分子量有機シリコン化合物により溶解抽出する工程を経て作製してもよい。すなわち、活物質、正極層3や負極層6の基材層となる高分子化合物、および可塑剤を含む高分子組成物を有機溶媒を用いてペースト化し、このペーストを製膜した後、この膜(層)状成形体から上述した低分子量有機シリコン化合物により可塑剤を溶解抽出し、その後非水溶液系電解液を含浸させることによって、正極層3や負極層6を形成してもよい。

【0049】上述したような製造方法を適用することによって、正極層3や負極層6に対する非水溶液系電解液の含浸量を高めることができるため、より一層電池特性の向上を図ることができる。さらに、上述した低分子量有機シリコン化合物は高分子組成物の層状成形体から可塑剤を溶解抽出する際に、この層状成形体に含まれる活物質の表面活性を向上させることから、活物質層にリチウムイオンをインターカレートあるいはデインターカレートしやすくなる。これによって、電池の内部インピーダンスを低減することが可能となることから、電池容量を十分に負荷に供給することが、すなわちいわゆる電池効率を向上させることができる。

【0050】上述した実施形態においては、本発明の製造方法を固体高分子電解質型のリチウム二次電池を製造する場合について説明したが、本発明はこれに限られるものではなく、イオン伝導タイプの固体高分子電解質型電池であれば種々の電池の製造に適用することができる。具体的には、(−) Li/LiAlCl<sub>4</sub>-SOC<sub>1</sub>/SOC<sub>1</sub>、(+) 等で示される塩化チオニルリチウム電池、(−) Li/MnO<sub>2</sub>、(+) 等で示されるリ



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チウムボタン電池（小型電池）、導電性高分子を用いたポリマー電池等の製造に適用することが可能である。

【0051】ところで、上記（1）式または（2）式で表される低分子量有機シリコン化合物は前述した特徴に加えて、本質的に低粘度であると共に、電池使用状態の温度範囲における粘度変化が小さく、さらに安定性が高く電池電圧での化学的な変化が少ないというような特徴を有している。すなわち、低分子量有機シリコン化合物は、通常の非水溶液系電池の酸化還元電位の高領域である5V程度においても安定で、電池反応に悪影響を及ぼす変化は示さず、さらには電極活物質の表面に作用して好ましい表面改質を与える。

【0052】従って、上述した本発明の製造方法の実施形態で述べたように、可塑剤の溶解抽出に使用した低分子量有機シリコン化合物が残存しても、電池特性に悪影響を及ぼすことはなく、さらには積極的に低分子量有機シリコン化合物を非水溶液系電解液の成分として使用することができる。本発明の電池用非水溶液系電解液は、上記したように低分子量有機シリコン化合物を必然的にもしくは積極的に含有する非水溶液系電解液組成物からなるものである。

【0053】低分子量有機シリコン化合物は、その低粘度でかつ粘度変化が小さいという特性を利用してイオン伝導性向上剤として非水溶液系電解液に含有させることができる。これによって、リチウムイオン等の金属イオンの移動性を高めることができ、かつその良好なイオン伝導性を安定に保つことができることから、温度依存性の少ない電池を得ることが可能となる。

【0054】このイオン伝導性向上剤としての低分子量有機シリコン化合物は、単に非水溶液系電解液の粘度低下に寄与するだけでなく、上記したように電極活物質の表面活性を高める作用をさらに有することから、正極層3および負極層6における金属イオンのインターカレーションおよびデインターカレーションのしやすさの向上にも寄与する。これによって、電池の内部インピーダンスを低下させることができ、電池効率の改善を図ることが可能となる。

【0055】さらに、低分子量有機シリコン化合物は安定性に優れ、上述したように電池電圧での化学的な変化が少なく、耐劣化性に富むことから、低分子量有機シリコン化合物を成分として用いた非水溶液系電解液を使用することによって、長期間使用しても特性劣化の少ない高品質の電池を得ることができる。

【0056】ここで、通常、非水溶液系電解液における非水系溶媒は、前述したように高誘電率を有する溶媒と低粘度の溶媒とを組合せた混合溶媒として使用される。低分子量有機シリコン化合物は、上述したようにイオン伝導性向上剤として従来の非水溶液系電解液に配合して用いることができ、この場合には上記した低粘性溶媒の一部として使用されることになるが、さらには低粘性

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溶媒の主体として用いることも可能である。この場合にも、低分子量有機シリコン化合物はイオン伝導性向上剤として機能することは言うまでもない。

【0057】上記したような低分子量有機シリコン化合物の使用形態のいずれにおいても、他の溶媒には低分子量有機シリコン化合物と相溶性に優れるものを使用することが好ましく、具体的には低分子量有機シリコン化合物は溶媒和係数（SP値）が5～6程度であるため、溶媒和係数（SP値）が4～13程度の炭化水素系有機溶媒を用いることが好ましい。これは溶媒和係数（SP値）の差があまり大きいと相溶性が低下するためであり、炭化水素系有機溶媒のより好ましい溶媒和係数（SP値）は5～10の範囲である。具体的には、高誘電率を有する溶媒としてはγ-ブチロラクトン（γ-BL）等が、また併用する低粘度溶媒としてはテトラヒドロフラン（THF）、2-メチルテトラヒドロフラン等が挙げられる。すなわち、低分子量有機シリコン化合物を配合した非水溶液系電解液としては、電解質、低分子量有機シリコン化合物、および溶媒和係数（SP値）が4～13程度（より好ましくは5～10程度）の炭化水素系有機溶媒とを含有する非水溶液系電解液組成物を用いることが好ましい。

【0058】非水溶液系電解液における低分子量有機シリコン化合物の配合量は3～95重量%の範囲とすることが好ましい。低分子量有機シリコン化合物の配合量が3重量%未満であると、当該低分子量有機シリコン化合物の低粘度特性が顕著に発揮され難く、一方95重量%を超えると配合溶剤組成系の誘電率が十分に維持され難いために電池用溶剤の品質にそぐわなくなる。特に、これら両者の特質を十分に発揮したバランスの良好な電池用溶剤とする上で、低分子量有機シリコン化合物の配合量は5～80重量%の範囲とすることが好ましい。

【0059】非水溶液系電解液の成分として用いる低分子量有機シリコン化合物は、（1）式で表される鎖状有機シリコン化合物、および（2）式で表される環状有機シリコン化合物のいずれであってもよいが、粘度がより低い鎖状有機シリコン化合物が好ましく用いられる。またこれらの混合物として使用する場合には、粘度がより低い鎖状有機シリコン化合物の環状有機シリコン化合物に対する配合比を95～10重量%の範囲とすることが好ましく、より好ましくは90～50重量%の範囲である。

【0060】上述したような低分子量有機シリコン化合物が必然的に含有された非水溶液系電解液、もしくは積極的に配合した非水溶液系電解液は、例えば前述した実施形態の固体高分子電解質型リチウム二次電池に好ましく用いられる。リチウム二次電池の具体的な構成は前述した通りであり、この低分子量有機シリコン化合物を含有する水溶液系電解液を用いたリチウム二次電池が本発明の固体高分子電解質型電池の実施形態となる。

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【0061】また、上記低分子量有機シリコン化合物を含有する水溶液系電解液は、可塑剤の介入の有無にかかわらず、前述した種々の固体高分子電解質型電池に使用することができ、またさらに固体高分子電解質型電池に限らず、各種の非水溶液系電池の電解液として用いることが可能である。

【0062】

【実施例】次に、本発明の具体的な実施例について説明する。

【0063】実施例1～2、比較例1～4

まず本発明の固体高分子電解質型電池の製造方法の実施例について説明する。正極の活性物質として $\text{LiCoO}_2$ で表されるリチウム含有コバルト酸化物（日本重化学工業（株）製）、導電性材料としてアセチレンブラック、非水溶液系電解液を保持しかつバインダとして機能する高分子化合物として（VdF-HFP）共重合体粉末（エルファトケム社製、Kynar 280L、VdF:HFPの共重合比は88:12）、および可塑剤としてジブチルフタレート（DBP）を用意し、これらを重量比で56:5:17:22となるように、溶剤としてのアセトン中で混合してペースト化した。このペーストを集電体としてのアルミニウムメッシュ上にナイフコートで塗布した後、上記溶剤を揮散させることによって、正極層となる厚さ約150 $\mu\text{m}$ の可塑剤含有層状成形体を作製した。

【0064】一方負極の活性物質としてメソフェーズピッチ系炭素繊維（（株）ベトカ製）、非水溶液系電解液を保持しかつバインダとして機能する高分子化合物として正極と同一の（VdF-HFP）共重合体粉末、および可塑剤として正極と同一のDBPを用意し、これらを重量比で58:17:25となるように、溶剤としてのアセトン中で混合してペースト化した。このペーストを集電体としての銅メッシュ上にナイフコートで塗布した後、上記溶剤を揮散させることによって、負極層となる厚さ約130 $\mu\text{m}$ の可塑剤含有層状成形体を作製した。

【0065】次に、上記した正極および負極と同様に、非水溶液系電解液を保持する高分子化合物としての（VdF-HFP）共重合体と可塑剤としてのDBPとを、重量比で50:50となるように、溶剤としてのアセトン中で混合してペースト化した。このペーストをガラス板上にナイフコートで塗布し、上記溶剤を揮散させた後、ガラス板から剥離して、固体高分子電解質層の基層となる厚さ約90 $\mu\text{m}$ の可塑剤含有層状成形体を作製した。

【0066】このようにして得た正極となる集電体および層状成形体、固体高分子電解質層となる層状成形体、負極となる層状成形体および集電体を、この順序で積層した後、40 $\mu\text{m}$ の熱ロールで圧着して、図1に示した電池セル8の元となる積層構造体を作製した。

【0067】次に、まず実施例1としてDBPの抽出溶媒にヘキサメチルシクロキサラン（MM）を用い、上記積層構造体を常温のMMに浸漬して、可塑剤であるDBP

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を溶解抽出して除去した。DBPの除去程度を紫外線分光光度の275 $\mu\text{m}$ 波長で追跡した結果、検出されなくなるまで時間は5～8分であった。

【0068】また、実施例2としてDBPの抽出溶媒にオクタメチルシクロキサラン（D4）を用い、同様に作製した積層構造体を常温のD4に浸漬して、可塑剤であるDBPを溶解抽出して除去した。DBPの除去程度を実施例1と同様に追跡した結果、検出されなくなるまで時間は7～10分であった。

10 【0069】本発明との比較例として、DBPの抽出溶媒にジエチルエーテル（比較例1）、メタノール（比較例2）、ヘキサン（比較例3）をそれぞれ用い、同様に作製した積層構造体を常温の各有機溶媒に浸漬して、可塑剤であるDBPを溶解抽出して除去した。DBPの除去程度を実施例1と同様に追跡した結果、検出されなくなるまで時間はそれぞれ10～15分、17～25分、30～40分であった。

【0070】上記したDBPの除去結果から明らかなように、実施例1のMMおよび実施例2のD4は極めてDBPの抽出能力に優れていることが分かる。これは、MMやD4が比較例の抽出溶媒に比べて表面張力が小さいことに起因しており、そのためにMMやD4は電池の積層構造体の内部深くにまで速やかに浸透し、これによってDBPを短時間で除去することができる。

【0071】また、DBPの抽出が完了した後は、抽出溶媒は積層構造体から速やかに揮散して残存させないことが必要である（ただし、本発明によるMM等の低分子量有機シリコン化合物の場合には残存しても問題ない）ため、DBPの除去終了後に室温に当該電池積層構造体を放置して、内部に抽出溶媒が残存しなくなるまでの時間を測定した。その結果、実施例1は15～20分、実施例2は17～22分、各比較例はそれぞれ10～15分、50～70分、120分以上であった。

【0072】このようにしてDBPを完全に除去した各実施例および各比較例の電池積層構造体に、エチレンカーボネート（EC）とジメチルカーボネート（DMC）とを容積比で2:1で混合した混合溶媒に常温で1mol/Lの1PF、電解質を溶解して調製した非水溶液系電解液をそれぞれ含浸した。この含浸速度は極めて速く、5分間では飽和含浸量に達するが、その後も少しは含浸するためにこの実施例では20分間浸漬して含浸させた。

【0073】このようにして得た面積4 $\text{cm}^2$ の各実施例および各比較例の電池セルについて、電解液の含浸率、イオン伝導度および内部インピーダンスを測定した。また、これら電解質を含浸させた各電池セルについて、1Cの充電電流で4.2Vまで充電した後、2.7Vまで1Cの電流で放電する充放電サイクルを繰り返し行い、1サイクル目の初期電池容量(mAh)、および10サイクル、50サイクル、100サイクル目の初期電池容量に対する各容量維持率を測定した。これらの測定結果を表1に示す。なお、





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表1に示した比較例4は、上記実施例においてDBPを \* [0074]  
用いない以外は同様にして電池セルを作製し、この電池 [表1]  
セルについて同様な測定を行ったものである。 \*

	DBP 抽出溶媒	電解液 含浸率 (%)	イオン 伝導度 (S/cm)	内部 インピーダンス ( $\Omega$ )	初期 容量 (mAh)	容量維持率(%)		
						100回	500回	1000回
実施例1	ヘキサメチルジシロキサン	65	$4.8 \times 10^{-2}$	57	18	97	82	90
実施例2	オクタメチルシクロテトラシロキサン	63	$4.5 \times 10^{-2}$	60	12	98	95	92
比較例1	メタノール	58	$8.1 \times 10^{-3}$	129	9	96	93	89
比較例2	メタノール	51	$2.0 \times 10^{-3}$	205	5	91	87	81
比較例3	ヘキサシロキサン	53	$2.5 \times 10^{-3}$	188	7	92	85	77
比較例4	(DBP無添加)	37	$6.2 \times 10^{-3}$	>500	2	76	40	12

表1から明らかなように、ヘキサメチルジシロキサン (MM) やオクタメチルシクロテトラシロキサン (D4) は高分子化合物を収縮させることがないことから、実施例1および実施例2では電解液の含浸率を大きくすることができ、よってイオン伝導度がよく、初期電池容量が大きく、充放電サイクル特性もよいことが分かる。また、電池の内部インピーダンスが低いのは、MMやD4による活物質表面の改質効果に基くもので、このために電池容量を十分に負荷に供給することができ、いわゆる電池効率に優れるものである。

【0075】これらに対して、比較例1～3による各抽出溶媒では、高分子化合物からDBPを抽出すると同時に当該高分子化合物を収縮させるために、その分イオン電解液の含浸量が減少して電池の初期電池容量が低く、充放電サイクル特性も悪い。また、電池の内部インピーダンスも実施例に比べて高いことが分かる。

【0076】なお、上記実施例1のMMに代えてオクタメチルトリシロキサン (MDM) やデカメチルテトラシロキサン (MD2M) を用いた場合についても同様な結果が得られ、また上記実施例2のD4に代えてデカメチルシクロペンタシロキサン (D5) を用いた場合についても同様な結果が得られた。

【0077】実施例3～4、比較例5

次に、本発明の固体高分子電解質型電池の実施例について説明する。

【0078】低分子量有機シリコン化合物としてヘキサメチルジシロキサン (MM) を用いて、これとメチルエチルカーボネート (MEC) とγ-ブチロラクトンとの混合重量比が 1:1の混合溶剤 (溶媒和係数 (SF値) = 9.5) とを、MMの配合比が上記混合溶剤に対して30重

量となるように混合し、この混合溶媒に常温で 1mol のLiPF<sub>6</sub>電解質を溶解して非水溶液系電解液 (実施例3) を調製した。

【0079】また、低分子量有機シリコン化合物としてオクタメチルシクロテトラシロキサン (D4) を用いて、これとジメチルカーボネートとスルホランとの重量比が2:1の液 (溶媒和係数 (SF値) = 10.2) とを、D4の配合比が45重量%となるように混合し、この混合溶媒に常温で 2mol のLiPF<sub>6</sub>電解質を溶解して非水溶液系電解液 (実施例4) を調製した。

【0080】さらに比較例5として、メチルエチルカーボネート (MEC) とγ-ブチロラクトンとを重量比で 1:1となるように混合し、この混合溶媒に常温で 1mol のLiPF<sub>6</sub>電解質を溶解して非水溶液系電解液を調製した。

【0081】上述した各実施例3、4および比較例5による各非水溶液系電解液を、上記実施例1、2および比較例1と同様にして作製した電池積層構造体にそれぞれ含浸 (含浸時間=20分) した。

【0082】このようにして得た面積 4cm<sup>2</sup> の各実施例および各比較例の電池セルについて、電解液の含浸率、イオン伝導度および内部インピーダンスを測定した。また、これら電解質を含浸させた各電池セルについて、1Cの充電電流で4.2Vまで充電した後、2.7Vまで1Cの電流で放電する充放電サイクルを繰り返し行い、1サイクル目の初期電池容量 (mAh)、および10サイクル、50サイクル、100サイクル目の初期電池容量に対する各容量維持率を測定した。これらの測定結果を表2に示す。

【表2】



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	電解液 含浸率 (wt%)	イオン 伝導度 (S/cm)	内部 インピーダンス (mΩ)	初期 容量 (mAh)	容量維持率(%)		
					10回	50回	100回
実施例3	70	$1.5 \times 10^{-2}$	61	12	97	95	90
実施例4	67	$9.6 \times 10^{-1}$	45	14	99	96	92
比較例5	63	$5.0 \times 10^{-4}$	165	8	97	94	82

表2から明らかなように、ヘキサメチルジシロキサン（MM）やオクタメチルシクロテトラシロキサン（D4）を配合した非水溶液系電解液を用いた電池は、イオン伝導度、内部インピーダンス、初期電池容量、充放電サイクル特性がいずれも優れていることが分かる。特に、実施例3および実施例4ではイオン伝導率が飛躍的に向上したために、2〜30の充放電を行っても電解質イオンの極端移動の追従性がよく、これにより急速充電並びに放電容量の大きな負荷への対応に幅の広がりが見られた。

【0083】

【発明の効果】以上説明したように、本発明の固体高分子電解質型電池の製造方法によれば、可塑剤の抽出効率等や非水溶液系電解液の含浸量を高めることができると共に、抽出溶媒が固体高分子電解質層内に残存しても電池系に悪影響を及ぼすことがない。これらによって、イ\*

\*イオン伝導性、内部インピーダンス、充放電サイクル特性等に優れた固体高分子電解質型電池を安定して得ることが可能となる。また、本発明の電池用非水溶液系電解液によれば、一層低粘性化や電極活物質の表面活性の向上等を図ることが可能となる。

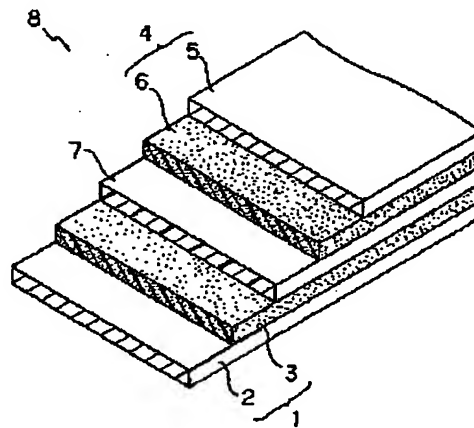
【図面の簡単な説明】

【図1】 本発明の一実施形態による固体高分子電解質型リチウム二次電池の要部構成を示す斜視図である。

【符号の説明】

- 1……正極
- 2、5……集電体
- 3……正極層
- 4……負極
- 6……負極層
- 7……固体高分子電解質層
- 8……電池セル

【図1】



フロントページの続き

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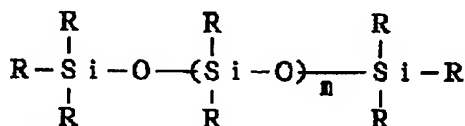
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 CLAIMS
 

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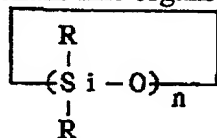
## [Claim(s)]

[Claim 1] The aforementioned plasticizer after fabricating the macromolecule constituent containing a plasticizer and the aforementioned high molecular compound in layers in the manufacture method of a solid-state polyelectrolyte type cell that opposite arrangement of a positive electrode and the negative electrode was carried out, through the solid-state polyelectrolyte layer which has a high-molecular-compound layer holding the nonaqueous-solution system electrolytic solution. [Formula 1]



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは0～7の整数を示す)

the chain-like organic silicon compound come out of and expressed -- and . [Formula 2]



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは3～10の整数を示す)

It is coming out and being chosen out of the annular organic silicon compound expressed that it is few. The manufacture method of the solid-state polyelectrolyte type cell characterized by having the process which carries out dissolution extraction using one sort of low-molecular-weight organic silicon compounds, and the process at which the aforementioned plasticizer sinks the aforementioned nonaqueous-solution system electrolytic solution into the aforementioned high-molecular-compound layer by which dissolution extraction was carried out, and forms the aforementioned solid-state polyelectrolyte layer in it.

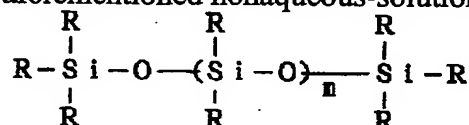
[Claim 2] It is being chosen out of the aforementioned positive electrode and a negative electrode in the manufacture method of a solid-state polyelectrolyte type cell according to claim 1 that it is few. The active material layer of one electrode After fabricating the macromolecule constituent containing the high molecular compound, active material, and plasticizer holding the aforementioned nonaqueous-solution system electrolytic solution in layers, The manufacture method of the solid-state polyelectrolyte type cell characterized by sinking in and forming the aforementioned nonaqueous-solution system electrolytic solution in the high-molecular-compound layer containing the aforementioned active material which carries out dissolution extraction of the aforementioned

plasticizer using the aforementioned low-molecular-weight organic silicon compound, and by which dissolution extraction of this plasticizer was carried out.

[Claim 3] The manufacture method of the solid-state polyelectrolyte type cell characterized by using the nonaqueous-solution system electrolytic-solution constituent containing the aforementioned low-molecular-weight organic silicon compound as the aforementioned nonaqueous-solution system electrolytic solution in the manufacture method of a solid-state polyelectrolyte type cell according to claim 1.

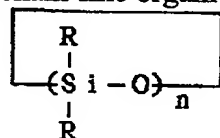
[Claim 4] The manufacture method of the solid-state polyelectrolyte type cell characterized by using a fluoride vinylidene or fluoride vinylidene-hexafluoropropylene copolymer as the aforementioned high molecular compound in the manufacture method of a solid-state polyelectrolyte type cell according to claim 1.

[Claim 5] It sets on the solid-state polyelectrolyte type cell possessing the solid-state polyelectrolyte layer which has a high-molecular-compound layer holding the nonaqueous-solution system electrolytic solution, and the positive electrode and negative electrode by which opposite arrangement was carried out through the aforementioned solid-state polyelectrolyte layer, and is the aforementioned nonaqueous-solution system electrolytic solution. [Formula 3]



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは0～7の整数を示す)

the chain-like organic silicon compound come out of and expressed -- and . [Formula 4]



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは3～10の整数を示す)

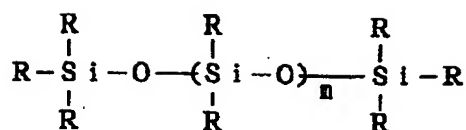
It is coming out and being chosen out of the annular organic silicon compound expressed that it is few. Solid-state polyelectrolyte type cell characterized by the bird clapper from the nonaqueous-solution system electrolytic-solution constituent which contains one sort of low-molecular-weight organic silicon compounds as an ion conductivity improver.

[Claim 6] In a solid-state polyelectrolyte type cell according to claim 5, an electrolyte, the aforementioned low-molecular-weight organic silicon compound, and a solvation coefficient (SP value) the aforementioned nonaqueous-solution system electrolytic-solution constituent Solid-state polyelectrolyte type cell characterized by containing the hydrocarbon system solvent of 4-13 at least.

[Claim 7] It is the solid-state polyelectrolyte type cell by which the aforementioned high-molecular-compound layer is characterized by the bird clapper from a fluoride vinylidene or fluoride vinylidene-hexafluoropropylene copolymer in a solid-state polyelectrolyte type cell according to claim 5.

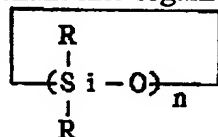
[Claim 8]

[Formula 5]



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは0～7の整数を示す)

the chain-like organic silicon compound come out of and expressed -- and . [Formula 6]



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは3～10の整数を示す)

It is coming out and being chosen out of the annular organic silicon compound expressed that it is few. The nonaqueous-solution system electrolytic solution for cells characterized by the bird clapper from the nonaqueous-solution system electrolytic-solution constituent which contains one sort of low-molecular-weight organic silicon compounds as an ion conductivity improver.

[Claim 9] In the nonaqueous-solution system electrolytic solution for cells according to claim 8, an electrolyte, the aforementioned low-molecular-weight organic silicon compound, and a solvation coefficient (SP value) the aforementioned nonaqueous-solution system electrolytic-solution constituent The nonaqueous-solution system electrolytic solution for cells characterized by containing the hydrocarbon system solvent of 4-13 at least.

[Claim 10] Setting to the nonaqueous-solution system electrolytic solution for cells according to claim 8, the aforementioned nonaqueous-solution system electrolytic-solution constituent is the aforementioned low-molecular-weight organic silicon compound. 3 - 95 % of the weight The nonaqueous-solution system electrolytic solution for cells characterized by containing in the range.

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**DETAILED DESCRIPTION**


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**[Detailed Description of the Invention]**
**[0001]**

[The technical field to which invention belongs] this invention relates to the nonaqueous-solution system electrolytic solution for cells used for the manufacture method of a solid-state polyelectrolyte type cell of having used the nonaqueous-solution system electrolytic solution, a solid-state polyelectrolyte type cell, and a nonaqueous-solution system cell.

**[0002]**

[Description of the Prior Art] It is indispensable to the electrolytic solution of the lithium cell which dislikes water in order to react violently with moisture from a standpoint with practical using the nonaqueous-solution system electrolytic solution, and such a lithium secondary battery is well known as a nonaqueous-solution system cell. Since the cell energy density is large, such a lithium secondary battery has been multiple-use-ized as a power supply of the cordless device which thinks small lightweight nature as important etc. Moreover, this cell function Development of the lithium ion solid-state polyelectrolyte type rechargeable battery provided as an about 0.5mm single cell of a super-thin shape (LPB), i.e., the cell using the organic high molecular compound which has the maintenance function of the nonaqueous-solution system electrolytic solution as a solid electrolyte layer, is also performed actively, and utilization level is reached. Although improvement of many component engineerings, such as selection, cell construction, etc. of the active material of a positive electrode and a negative electrode, has contributed to utilization of these rechargeable batteries, selection of the electrolytic solution is expected much more improvement in technical.

[0003] Here, the strong-base solution of a potassium hydroxide is used for the electrolytic solution of a solution system cell. the liquid property that the operation effect of the electrolytic solution over a cell reaction here is the hypoviscosity of water, and is large, and the good ionic conduction nature of about 10 to 2 or more ohm/cm by the potassium hydroxide as solution have realized exertion of a practical cell capacity required for a cell, and correspondence to a big load [ of specific inductive capacity ] On the other hand, by the nonaqueous-solution system cell, the present condition is racking one's brains for maintaining big ionic conduction nature compared with the solution system electrolytic solution stably, by the use potential difference of a cell, since there are few low liquids (solvent) of viscosity. It is 50 % of the weight about the ion electrolyte content in the solid-state polyelectrolyte layer especially used in a LPB type. If it is not made a grade above, also theoretically and experimentally, it is checked that a fully practical cell is not obtained.

[0004] In order to raise the content of the electrolyte in a solid-state polyelectrolyte layer, some methods are tried from the former. The technology As one, the method using the high molecular compound which includes hetero atom teams, such as alkylene oxide, in the molecular structure as a solid-state polyelectrolyte layer is mentioned (refer to Japanese Patent Publication No. 6 No. -52671 official report). Such a solid-state polyelectrolyte layer is 50 % of the weight about an electrolyte. It is known that it is possible to make it sink in above. However, since the hetero atom team which sank in the electrolyte becomes a sea phase in the macromolecule structure which constitutes a solid-state



polyelectrolyte layer and the macromolecule principal chain except a hetero atom team forms the discontinuous phase, the fluidity of a discontinuous phase will increase an electrolyte, so that it high-sinks in. That is, the present condition is being unable to make [ many / that the electrolytic amount of sinking in is expected in order to present long-term use with an electrolyte as a practical cell from a bird clapper as a configuration is unstable so that it high-sinks in / so ] it.

[0005] As other methods, it is for example, the U.S. \*\*\*\*\*. There is technology which sinks an electrolyte into this amorphous phase using the high molecular compound with which the crystal phase and the amorphous phase were intermingled as a solid-state polyelectrolyte layer as indicated by No. 5,456,000. although the instability of configuration maintenance which is seen in the solid-state polyelectrolyte layer which has the hetero atom team of the above-mentioned [ this technology ] is avoidable practically -- electrolytic rate of impregnation -- at most 30 - 40 % of the weight Since it is a grade, like  $10^{-5}$  -  $10^{-4}$  ohm/cm, only a degree is obtained but it passes over ionic conductivity low as a practical use cell.

[0006] For this reason, the above-mentioned U.S. \*\*\*\*\* In No. 5,456,000 The fluoride vinylidene-hexafluoropropylene copolymer used as a polyelectrolyte A plasticizer like a dibutyl phthalate, dimethyl phthalate, and tris-butoxy ethyl phosphate is blended with polymeric materials like (describing it as a copolymer (VdF-HFP) hereafter). A film is produced using the raw material which blended this plasticizer, and a lower alcohol like ethanol, diethylether, a tetrahydrofuran, and the technology that sinks in the nonaqueous-solution system electrolytic solution containing an electrolyte after passing and carrying out extraction removal with a low boiler like Korean geisha are indicated in the plasticizer out of this film. By applying such a method, it is 60 - 70 % of the weight about the rate of impregnation of the nonaqueous-solution system electrolytic solution. It can carry out and it is shown that ionic conductivity improves to  $10^{-2}$  -  $10^{-3}$  ohm/cm.

[0007] When adopting the above-mentioned method, it is necessary to remove a plasticizer completely by the fuel cell subsystem in order to start an oxidation-reduction reaction with the operating potential of a cell. However, it had the problem that the conventional extracting solvent which was mentioned above has the solubility of a plasticizer, and the inadequate diffusion permeability inside a high molecular compound, and full extraction of a plasticizer takes it for a long time, and a problem which is referred to as having a bad influence on a fuel cell subsystem in response to oxidation reduction by the cell busy condition when an extracting solvent remains in a solid-state polyelectrolyte layer again. Furthermore, while each conventional extracting solvent mentioned above carried out dissolution extraction of the plasticizer, it shrank the high molecular compound used as a solid-state polyelectrolyte layer, and it had the fault of reducing the amount of sinking in of the nonaqueous-solution system electrolytic solution. Moreover, when the work environment of the dissolution extraction process of a plasticizer etc. is taken into consideration, an extracting solvent is wanted to have the property of not checking earth environment as it is safe to a human body and is observed further recently.

[0008] On the other hand, an improvement aiming at much more improvement in charge-and-discharge efficiency etc. is desired about the nonaqueous-solution system electrolytic solution itself. That is, the nonaqueous-solution system electrolytic solution consists of ionicity compounds (electrolyte) which are dissolved in an organic solvent and it and perform ionic migration in it. Among these, in addition to being a high dielectric constant, an organic solvent is asked for it being the low viscosity which makes ionic conduction easy in the operation temperature of a cell so that internal impedance of a cell may not be raised. Although high dielectric constant matter, such as ethylene carbonate, is used for the solvent of the conventional nonaqueous-solution system electrolytic solution, it is a solid-state, and the electrolytic solution actual since there are many liquids with high viscosity is mixed with the solvent of hypoviscosity, apparent electrolytic-solution viscosity is made low, and it is made not to spoil the mobility of a metal ion in ordinary temperature. Moreover, the solvent of hypoviscosity is expected to be the liquid which may raise the surface activity of an active material to an electrode active material layer in order to make metal ions, such as

a lithium ion, easy to intercalate or deintercalate.

[0009] As a solvent of hypoviscosity with which a property which was mentioned above is demanded, although chain-like carbonate, such as dimethyl carbonate and JIEME chill carbonate, etc. is used conventionally, when aiming at improvement in a cell property, the solvent which can raise the surface activity of much more reduction in the viscosity of the nonaqueous-solution system electrolytic solution or an electrode active material is called for.

[0010]

[Problem(s) to be Solved by the Invention] As mentioned above, in the manufacturing process of the solid-state polyelectrolyte layer of the nonaqueous-solution system cell which used the conventional plasticizer together, the extracting solvent of a plasticizer which has a property as shown below is called for. That is, even if the vapor pressure in the extraction temperature which does not shrink a high molecular compound at the time of the extraction of a plasticizer which carries out diffusion osmosis promptly to the interior of the high molecular compound which solubility with a plasticizer is large, and surface tension is small, and constitutes a solid-state polyelectrolyte layer should vaporize promptly greatly and should further remain in a high-molecular-compound layer, while it is safe for the human body which does not have a bad influence on a fuel cell subsystem, an extracting solvent of a plasticizer which does not check earth environment and which has the property of \*\* is desired

[0011] Moreover, about the nonaqueous-solution system electrolytic solution itself, while an improvement aiming at improvement in charge-and-discharge efficiency etc. is desired and specifically being able to form the nonaqueous-solution system electrolytic solution into low viscosity further, the solvent which can raise the surface activity of an electrode active material is called for.

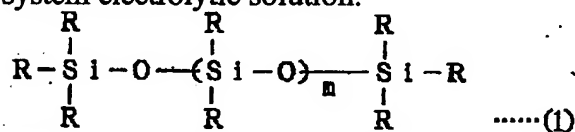
[0012] In case this invention was made in order to cope with such a technical problem, uses a plasticizer together and manufactures the solid-state polyelectrolyte type cell using the nonaqueous-solution system electrolytic solution, while it raises the amount of sinking in of the extraction efficiency of a plasticizer, etc. and the nonaqueous-solution system electrolytic solution It aims at offering the manufacture method of a solid-state polyelectrolyte type cell and solid-state polyelectrolyte type cell which do not have a bad influence on a fuel cell subsystem even if an extracting solvent should remain in a solid-state polyelectrolyte layer. It aims at offering the nonaqueous-solution system electrolytic solution for cells which furthermore aimed at reduction in viscosity, and improvement in the surface activity of an electrode active material further.

[0013]

[Means for Solving the Problem] The result which advanced examination about various solvents in order to attain the above-mentioned purpose, the low-molecular-weight chain-like organic silicon compound expressed with the following (1) formula -- and -- The low-molecular-weight annular organic silicon compound expressed with (2) formulas Are the right solution of the plasticizer used for (a) cell formation, dissolve almost all plasticizers easily and carry out extraction removal. Even if (b) surface tension compares with the conventional extraction solution 15 dyn/cm order, are small. It is easy to permeate the detailed portion of a cell composition constituent quickly. Do not shrink a high molecular compound at the time of extraction of the (c) plasticizer. (d) The vapor pressure in extraction temperature vaporizes promptly greatly. Earth environment is not spoiled while it is very safe for the (e) human body. It has the various properties for which the extracting solvent of the plasticizer at the time of using a plasticizer together and manufacturing a solid-state polyelectrolyte layer is asked, and adds to it. (f) While being essentially hypoviscosity The viscosity change in the temperature requirement of a cell busy condition is small, is stabilized in the volatility of a metal ion, and can raise. There was little change chemical under (g) cell service condition, and while not having a bad influence on a fuel cell subsystem, it found out having various properties for which the hypoviscosity solvent of the nonaqueous-solution system electrolytic solution is asked, such as being rich in degradation-proof nature.

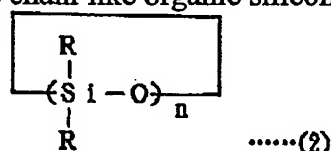
[0014] It is [Formula 7] about the aforementioned plasticizer as the manufacture method of the solid-

state polyelectrolyte type cell of this invention was indicated to the claim 1, after having accomplished this invention based on knowledge which was described above, and fabricating the macromolecule constituent containing a plasticizer and the aforementioned high molecular compound in layers in the manufacture method of a solid-state polyelectrolyte type cell that opposite arrangement of a positive electrode and the negative electrode was carried out, through the solid-state polyelectrolyte layer which has a high-molecular-compound layer holding the nonaqueous-solution system electrolytic solution.



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは0～7の整数を示す)

The chain-like organic silicon compound come out of and expressed, and [Formula 8]



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは3～10の整数を示す)

It is coming out and being chosen out of the annular organic silicon compound expressed that it is few. It is characterized by having the process which carries out dissolution extraction using one sort of low-molecular-weight organic silicon compounds, and the process which sinks the aforementioned nonaqueous-solution system electrolytic solution into the aforementioned high-molecular-compound layer by which dissolution extraction of the aforementioned plasticizer was carried out, and forms the aforementioned solid-state polyelectrolyte layer.

[0015] Moreover, the solid-state polyelectrolyte layer which has the high-molecular-compound layer in which the solid-state polyelectrolyte type cell of this invention held the nonaqueous-solution system electrolytic solution, In the solid-state polyelectrolyte type cell possessing the positive electrode and negative electrode by which opposite arrangement was carried out through the aforementioned solid-state polyelectrolyte layer the aforementioned nonaqueous-solution system electrolytic solution the above The chain-like organic silicon compound expressed with (1) formula, and the above it is chosen out of the annular organic silicon compound expressed with (2) formulas -- at least -- One sort of low-molecular-weight organic silicon compounds It is characterized by the bird clapper from the nonaqueous-solution system electrolytic-solution constituent contained as an ion conductivity improver.

[0016] furthermore, the nonaqueous-solution system electrolytic solution for cells of this invention -- the above The chain-like organic silicon compound expressed with (1) formula, and the above it is chosen out of the annular organic silicon compound expressed with (2) formulas -- at least -- It is characterized by the bird clapper from the nonaqueous-solution system electrolytic-solution constituent which contains one sort of low-molecular-weight organic silicon compounds as an ion conductivity improver.

[0017]

[Embodiments of the Invention] Hereafter, the form for carrying out this invention is explained.

[0018] 1 operation form which applied the manufacture method of the solid-state polyelectrolyte type cell of this invention to the manufacture method of the lithium secondary battery of a nonaqueous-solution system is explained. Before explaining the manufacture method in full detail, the

composition of the rechargeable battery of a nonaqueous-solution system lithium is first explained with reference to drawing 1. In addition, this lithium secondary battery is 1 operation form of the solid-state polyelectrolyte type cell of this invention, and this invention is not limited to this.

[0019] Drawing 1 shows, solid-state polyelectrolyte type the important section, i.e., the cell portion, of a lithium secondary battery of this operation gestalt, and 1 is the positive electrode which carried out laminating formation and constituted the positive-electrode layer 3 on the charge collector 2. Moreover, 4 is the negative electrode which carried out laminating formation and constituted the negative-electrode layer 6 on the charge collector 5, and it is arranged so that the negative-electrode layer 6 of this negative electrode 4 may counter with the positive-electrode layer 3 of a positive electrode 1. Between these positive electrodes 1 and the negative electrode 4, it intervenes so that the solid-state polyelectrolyte layer 7 may be located between the positive-electrode layer 3 and the negative-electrode layer 6. The cell 8 is constituted by these and a solid-state polyelectrolyte type lithium secondary battery is constituted by holding a winding object, a layered product, etc. of this cell 8 in a cell container.

[0020] The above-mentioned positive electrode 1 has the structure which supported with the charge collector 2 the positive-electrode layer 3 as a barrier layer which consists of high molecular compounds holding an active material, the nonaqueous-solution system electrolytic solution, and this electrolytic solution. here -- the various oxides  $2O_4$  as an active material, for example,  $LiMn$ , etc. -- a lithium manganese multiple oxide and  $LiNiO_2$  etc. -- a lithium content nickel oxide and  $LiCoO_2$  etc. -- cull GEKON compounds containing a lithium content cobalt oxide, a lithium content nickel cobalt oxide, and a lithium, such as for example, an amorphous vanadium pentoxide, etc. 2 titanium sulfides, and molybdenum disulfide, etc. can be mentioned Especially, a lithium manganese multiple oxide, a lithium content cobalt oxide, and a lithium content nickel oxide are preferably used for a top with little degradation by electric field from the efficiency of the charge which can be used as a cell being good.

[0021] The nonaqueous-solution system electrolytic solution mentioned above is adjusted by dissolving an electrolyte in non-drainage system solvents, such as an organic solvent. As a non-drainage system solvent, ethylene carbonate (EC), propylene carbonate (PC), Butylene carbonate (BC), dimethyl carbonate (DMC), Diethyl carbonate (DEC), ethyl methyl carbonate (EMC), gamma - A butyrolactone (gamma-BL), a sulfolane, an acetonitrile, 1, 2-dimethoxyethane, 1, 3-dimethoxypropane, a wood ether, organic solvents generally used as the electrolytic solution for cells, such as a tetrahydrofuran (THF) and 2-methyl tetrahydrofuran, -- in addition, it mentioned above (1) formula -- or -- The low-molecular-weight organic silicon compound expressed with (2) formulas can be mentioned.

[0022] Usually, a non-drainage system solvent is used as a mixed solvent which combined the solvent which has a high dielectric constant, and the solvent of hypoviscosity, and a low-molecular-weight organic silicon compound can be used as a kind of a low viscosity solvent etc. In addition, the low-molecular-weight organic silicon compound used as a kind of this low viscosity solvent etc. and the nonaqueous-solution system electrolytic-solution constituent using this are explained in full detail behind.

[0023] Moreover, as the above-mentioned electrolyte, the lithium salt of a lithium perchlorate ( $LiClO_4$ ), a 6 fluoride [ phosphoric-acid ] lithium ( $LiPF_6$ ), hoe 4 lithium fluoride ( $LiBF_4$ ), a 6 fluoride arsenic lithium ( $LiAsF_6$ ), a trifluoromethane sulfonic-acid lithium ( $LiCF_3 SO_3$ ), a screw trifluoromethyl SURUHOMECHIRUHONIRUIMIDO lithium [ $LiN (CF_3 SO_3)_2$ ], etc. is mentioned, for example. The amount of dissolutions to the non-drainage system solvent of these electrolytes It is desirable to consider as about 0.2-2 mol/L.

[0024] An alkylene-oxide system high molecular compound like fluorine system high molecular compounds, such as a fluoride vinylidene and fluoride vinylidene-hexafluoropropylene copolymer (VdF-HFP) (copolymer), and a polyethylene oxide as a high molecular compound holding the nonaqueous-solution system electrolytic solution which was mentioned above etc. can be mentioned.

In this case, it does not use independently as a binder of an active material, and (VdF-HFP) does not bar mixing with a copolymer and using polyvinylidene fluoride and a fluorine system high molecular compound like a polytetrafluoroethylene.

[0025] When producing by the same method as the solid-state polyelectrolyte layer 7 which mentions the positive-electrode layer 3 as a barrier layer later among the above-mentioned high molecular compounds, it is desirable to use a fluoride vinylidene and a copolymer (VdF-HFP). In addition, in order to give conductivity to the positive-electrode layer 3, carbon black, such as an artificial graphite and acetylene black, nickel powder, etc. can be used together.

[0026] Moreover, as a charge collector 2 of a positive electrode 1, the foil of aluminum or nickel, a mesh, an expanded metal, punched metal, etc. are used, for example.

[0027] The negative electrode 4 has the structure which supported with the charge collector 5 the negative-electrode layer 6 as an active material layer which consisted of high molecular compounds holding an active material, the nonaqueous-solution system electrolytic solution, and this electrolytic solution etc., and it is arranged through the solid-state polyelectrolyte layer 7 so that the negative-electrode layer 6 may counter with the positive-electrode layer 3 of a positive electrode 1. Although the basic structure of a negative electrode 4 and a part of material of construction are similar with the positive electrode 1 mentioned above, a positive electrode 1 and the material in which it differs are the active material which intercalates a lithium ion, and the quality of the material of a charge collector 5.

[0028] That is, in a lithium ion, it is possible occlusion and to emit, namely, to intercalate and deintercalate to the active material which is one of the components of the negative-electrode layer 6, for example, carbonaceous material is used for it. The carbonaceous material represented by what calcinates organic high molecular compounds, such as phenol resin, a polyacrylonitrile, and a cellulose, for example, and obtained as this carbonaceous material, the thing which calcinates corks and a pitch and is obtained, artificial graphite, natural graphite, etc. can be mentioned. Especially, it is under an ordinary pressure or reduced pressure in inert gas atmosphere, such as an argon and nitrogen. It is known that the mezzo-soprano carbon which calcinates the above-mentioned organic high molecular compound, and is obtained at the temperature of 773-3273K is excellent in the intercalation property of a lithium ion. In order to aim at conductive improvement, of course, you may use KETCHIEN black, carbon black, etc. together.

[0029] Moreover, as a charge collector 5 of a negative electrode 4, it replaces with the aluminum in a positive electrode 1 etc., and the thing of the appearance configuration of the positive-electrode charge collector 2 and the same configuration is used using copper etc. In addition, the same thing as the positive-electrode layer 3 is used for the high molecular compound which is one of the components of the negative-electrode layer 6. Moreover, it is as having mentioned above about the nonaqueous-solution system electrolytic solution.

[0030] The solid-state polyelectrolyte layer 7 arranged between the positive electrodes 1 and negative electrodes 4 which were mentioned above consists of high molecular compounds holding the nonaqueous-solution system electrolytic solution which was mentioned above, and this electrolytic solution. That is, the solid-state polyelectrolyte layer 7 is constituted by making the nonaqueous-solution system electrolytic solution sink in and hold in the high-molecular-compound layer which has the maintenance function of the nonaqueous-solution system electrolytic solution. in this invention, when forming a high-molecular-compound layer so that it may explain in full detail behind, the plasticizer was used together, and this plasticizer was mentioned above (1) formula -- or -  
- The nonaqueous-solution system electrolytic solution is high-infiltrated into a high-molecular-compound layer by carrying out extraction removal by the low-molecular-weight organic silicon compound expressed with (2) formulas.

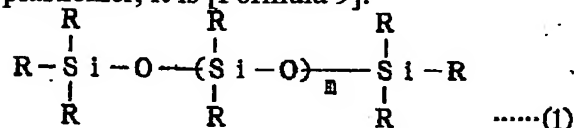
[0031] As a high molecular compound used as the subject of the solid-state polyelectrolyte layer 7, fluorine system high molecular compounds, such as a fluoride vinylidene and a copolymer (VdF-HFP), are used, and the copolymer which is excellent in the maintenance function of the nonaqueous-

solution system electrolytic solution especially mentioned above (VdF-HFP) is used preferably. In this (VdF-HFP) copolymer, especially a fluoride vinylidene contributes to improvement in a mechanical strength in the frame section of a copolymer, and hexafluoropropylene is incorporated in the state amorphous to a copolymer, and it functions as maintenance of the nonaqueous-solution system electrolytic solution, and the transparency section of a lithium ion. It is as having mentioned above about the nonaqueous-solution system electrolytic solution which sinks into the base-material layer of the solid-state polyelectrolyte layer 7 which consists of such a high molecular compound. [0032] Next, the manufacture method of the solid-state polyelectrolyte type lithium secondary battery mentioned above is explained.

[0033] First, the production method of the solid-state polyelectrolyte layer 7 which is one of the features of this invention is described. That is, a plasticizer (plasticity solvent) is blended with fluorine system high molecular compounds mentioned above, such as a fluoride vinylidene and a copolymer (VdF-HFP), and the macromolecule constituent used as the formation material of a high-molecular-compound layer is prepared.

[0034] Here, as the above-mentioned plasticizer, a dibutyl phthalate (DBP), dimethyl phthalate (DMP), diethyl phthalate (DEP), propylene carbonate (PC), tris-butoxy ethyl phosphate, etc. are used. Moreover, it sets to the above-mentioned macromolecule constituent, and the loadings of these plasticizers are 20 - 70 % of the weight. Considering as the range is desirable. The loadings of a plasticizer are 20 % of the weight. There is a possibility that the amount of maintenance of the nonaqueous-solution system electrolytic solution may be insufficient in it being the following, and sufficient ion conductivity may not be obtained, and, on the other hand, the loadings of a plasticizer are 70 % of the weight. If it exceeds, configuration maintenance ability, intensity, etc. of a high-molecular-compound layer used as the base-material layer of the solid-state polyelectrolyte layer 7 will fall. It is 50 - 70 % of the weight about the loadings of a plasticizer since the dissolution extraction efficiency of a plasticizer uses a high low-molecular-weight organic silicon compound so that it may mention later in this invention especially. Even if it makes it the range and a large quantity, generating of a plasticizer residue can be prevented effectively. That is, the nonaqueous-solution system electrolytic solution can be high-infiltrated into a high-molecular-compound layer. [0035] It is made to dissolve in an organic solvent, the macromolecule constituent containing a high molecular compound which was described above, and a plasticizer is pasted, and this macromolecule constituent paste is fabricated in layers. Specifically, after producing a macromolecule constituent paste for example, by the knife coating machine, an organic solvent is vaporized and the stratified Plastic solid of a macromolecule constituent is produced. This stratified Plastic solid may be formed independently, and may be produced as a layered product with a positive electrode 1 or a negative electrode 4.

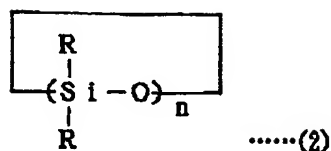
[0036] Next, dissolution extraction of the plasticizer contained in the stratified Plastic solid of the above-mentioned macromolecule constituent is carried out. In dissolution extraction of this plasticizer, it is [Formula 9].



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは0～7の整数を示す)

The chain-like organic silicon compound come out of and expressed, and [Formula 10]





(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは3~10の整数を示す)

It is coming out and being chosen out of the annular organic silicon compound expressed that it is few. One sort of liquefied low-molecular-weight organic silicon compounds are used.

[0037] the above (1) formula -- and -- As R group in (2) formulas Alkyl groups, such as a methyl group, an ethyl group, a propyl group, a butyl, and an octyl machine, Alkenyl machines, such as aryl groups, such as a phenyl group and a tolyl group, a vinyl group, and an allyl group, beta - A phenylethyl machine, gamma - Unsubstituted [ of aralkyl machines, such as a phenylpropyl machine, etc. ] A univalent organic machine, And the hydrogen atom combined with the carbon atom of these bases was replaced by a halogen atom, a cyano group, a hydroxyl group, the carboxyl group, the carbonyl group, the amino group, the alkoxy group, etc. A univalent organic machine is illustrated. Especially, a methyl group and a phenyl group are preferably used from points, such as stability, and a methyl group is especially desirable from points, such as volatility.

[0038] Moreover, it mentioned above. m in (1) formula It is the integer of 0-7. n in (2) formulas is the integer of 3-10. If the range which m and n described above is exceeded, viscosity, volatility, stability, etc. will fall. when hypoviscosity, good stability, etc. obtain especially m and n -- m considering as the range of 0-5 -- moreover, n It is desirable to consider as the range of 3-7. As the above-mentioned example of a low-molecular-weight organic silicon compound Hexa methyl disiloxane (MM), octamethyl trisiloxane (MDM), Chain-like poly methyl siloxanes, such as a decamethyl tetrapod siloxane (MD2M) Annular poly methyl siloxanes, such as octamethylcyclotetrasiloxane (D4) and decamethyl cyclopentasiloxane (D5), The compound which furthermore denaturalized all these all [ a part or ] with other alkyl groups, a phenyl group, an aralkyl machine, an alkoxy group, an ester machine, the amino group, the epoxy group, the halogenation machine, etc. is mentioned.

[0039] Extraction of the plasticizer by low-molecular-weight organic silicon compound which was mentioned above can \*\*\*\* the stratified Plastic solid of the macromolecule constituent containing a plasticizer to a low-molecular-weight organic silicon compound (liquid), or can be carried out by various methods, such as exposing the stratified Plastic solid of the macromolecule constituent which contains a plasticizer in the steam bath of a low-molecular-weight organic silicon compound.

Moreover, in case it \*\*\*\* to a low-molecular-weight organic silicon compound, warming, rocking, ultrasonic irradiation, etc. can also be used together.

[0040] the interior of the stratified Plastic solid of that various plasticizers may be dissolved in the extracting solvent of a plasticizer which was mentioned above good here, and a macromolecule constituent -- deep -- alike -- until -- that it permeates promptly and a plasticizer may be dissolved efficiently, vaporizing promptly after dissolution extraction of a plasticizer and not remaining, etc. are called for In addition, it is the property currently searched for in order for the prompt vaporization after dissolution extraction of a plasticizer to receive oxidation reduction by the cell voltage if the conventional plasticizer extracting solvent remains, and to have a bad influence on a cell property.

[0041] To the demand characteristics to such a plasticizer extracting solvent, the feature with which it is [ on the physical properties of the low-molecular-weight organic silicon compound mentioned above ] common is the right solution of a plasticizer which was first described above to the 1st, therefore can dissolve almost all plasticizers easily, and can carry out extraction removal of this efficiently.

[0042] Even if surface tension compares [ 2nd ] with the conventional extracting solvent 15 dyn/cm

order, it is small, and the interior, a detailed portion, etc. of a stratified Plastic solid of a macromolecule constituent are permeated quickly, and extraction removal of the plasticizer can be carried out in a short time. In case the solid-state polyelectrolyte layer 7 is especially processed and produced as a layered product with a positive electrode 1 or a negative electrode 4, the good permeability of a low-molecular-weight organic silicon compound demonstrates an effect further.

[0043] Since it excels in volatility, after dissolution extraction of a plasticizer, it vaporizes promptly, and the extraction process of a plasticizer can be carried [ 3rd ] out efficiently. However, since it does not have a possibility of having a bad influence on a cell property even if the low-molecular-weight organic silicon compound mentioned above remains in the solid-state polyelectrolyte layer 7 and it not only does not do a bad influence, but contributes to low viscosity-ization of the nonaqueous-solution system electrolytic solution, i.e., the improvement in ionic conductivity, so that it may explain in full detail behind, improvement in a cell property can be aimed at.

[0044] Furthermore, in case the low-molecular-weight organic silicon compound which was mentioned above in addition to the feature which was described above carries out dissolution extraction of the plasticizer from the stratified Plastic solid of a macromolecule constituent, it does not almost shrink the high molecular compound used as the base material of the solid-state polyelectrolyte layer 7. This enables it to sink in more nonaqueous-solution system electrolytic solutions. This contributes to the improvement of ionic conductivity. Moreover, to a human body, environment, etc., since it is very safe, the low-molecular-weight organic silicon compound mentioned above also has the advantage of not spoiling the fabrication operation environment and the earth environment of a cell.

[0045] it mentioned above -- as -- dissolution extraction of the plasticizer from the stratified Plastic solid of a macromolecule constituent (1) formula -- or -- By using the low-molecular-weight organic silicon compound expressed with (2) formulas, it becomes possible to carry out extraction removal of the plasticizer efficiently for a short time, without making a plasticizer remain. Moreover, the low-molecular-weight organic silicon compound used for dissolution extraction will not have a bad influence on a cell property, even if it vaporizes for a short time and a low-molecular-weight organic silicon compound remains. Furthermore, in order not to almost shrink a high molecular compound, it becomes possible to infiltrate more nonaqueous-solution system electrolytic solutions.

[0046] The high-molecular-compound layer which carried out dissolution extraction of the plasticizer by the low-molecular-weight organic silicon compound turns into a base-material layer of the solid-state polyelectrolyte layer 7. And the solid-state polyelectrolyte layer 7 is obtained by infiltrating the nonaqueous-solution system electrolytic solution into this high-molecular-compound layer. The amount of sinking in of the nonaqueous-solution system electrolytic solution to a high-molecular-compound layer is 20 - 70 % of the weight, as mentioned above. The range, especially 50 - 70 % of the weight Considering as the range is desirable.

[0047] Next, the production method of a positive electrode 1 and a negative electrode 4 is described. In production of a positive electrode 1, the above-mentioned high molecular compound mixes a conductive material to a meltable organic solvent the active material first mentioned above, the high molecular compound holding the nonaqueous-solution system electrolytic solution, and if needed, and a paste is adjusted. Subsequently, the non-sunk in electrolytic-solution positive-electrode layer 3 is obtained by producing this paste. The laminating of this is carried out to a charge collector 1, and a positive electrode 1 is obtained by infiltrating the nonaqueous-solution system electrolytic solution into this. Or the above-mentioned paste can be applied to a charge collector 2, and the nonaqueous-solution system electrolytic solution can be infiltrated into this. After producing a layered product with the solid-state polyelectrolyte layer 7, you may carry out sinking [ of the nonaqueous-solution system electrolytic solution ] in. In addition, the negative electrode 4 as well as a positive electrode 1 is produced fundamentally.

[0048] Here, you may produce the positive-electrode layer 3 and the negative-electrode layer 6 which are an active material layer through the process which carries out dissolution extraction by the low-



molecular-weight organic silicon compound which mentioned the plasticizer above while using the macromolecule constituent which blended the plasticizer like the solid-state polyelectrolyte layer 7 mentioned above. That is, you may form the positive-electrode layer 3 and the negative-electrode layer 6 by carrying out dissolution extraction of the plasticizer by the low-molecular-weight organic silicon compound mentioned above from this film (layer)-like Plastic solid after pasting the active material, the high molecular compound used as the base-material layer of the positive-electrode layer 3 or the negative-electrode layer 6, and the macromolecule constituent containing a plasticizer using the organic solvent and producing this paste, and infiltrating the nonaqueous-solution system electrolytic solution after that.

[0049] Since the amount of sinking in of the nonaqueous-solution system electrolytic solution to the positive-electrode layer 3 or the negative-electrode layer 6 can be raised by applying the manufacture method which was mentioned above, improvement in a cell property can be aimed at further.

Furthermore, since the low-molecular-weight organic silicon compound mentioned above raises the surface activity of the active material contained in this stratified Plastic solid in case it carries out dissolution extraction of the plasticizer from the stratified Plastic solid of a macromolecule constituent, about a lithium ion, it intercalates, or is easy to deintercalate and it becomes an active material layer. By this, it can raise fully supplying cell capacity to a load from a bird clapper as it is possible to reduce the internal impedance of a cell, i.e., the so-called cell efficiency.

[0050] In the operation gestalt mentioned above, although the manufacture method of this invention was explained about the case where a solid-state polyelectrolyte type lithium secondary battery is manufactured, this invention is not restricted to this, and if it is an ionic conduction type solid-state polyelectrolyte type cell, it is applicable to manufacture of various cells. Specifically, they are (-) Li/LiAlCl<sub>4</sub>-SOCl<sub>2</sub> / SOCl<sub>2</sub>. The thionyl chloride lithium cell shown by (+) etc., and (-) Li/MnO<sub>2</sub> It is possible to apply to manufacture of the lithium button cell (small cell) shown by (+) etc., the polymer battery using the conductive polymer, etc.

[0051] by the way, the above (1) formula -- or -- the feature which the low-molecular-weight organic silicon compound expressed with (2) formulas mentioned above -- in addition, while being essentially hypoviscosity, the viscosity change in the temperature requirement of a cell busy condition is small, and it has the feature which stability says further that it is high and there is little chemical change by the cell voltage That is, a low-molecular-weight organic silicon compound is stable also in about [ which is the high field of the oxidation reduction potential of the usual nonaqueous-solution system cell ] 5V, and change which has a bad influence on a cell reaction is not shown, but acts on the front face of an electrode active material further, and gives a desirable surface treatment.

[0052] Therefore, as the operation gestalt of the manufacture method of this invention mentioned above described, even if the low-molecular-weight organic silicon compound used for dissolution extraction of a plasticizer remains, it cannot have a bad influence on a cell property, and a low-molecular-weight organic silicon compound can be used as one component of the nonaqueous-solution system electrolytic solution still more positively. The nonaqueous-solution system electrolytic solution for cells of this invention consists of a nonaqueous-solution system electrolytic-solution constituent which contains a low-molecular-weight organic silicon compound inevitably or positively as described above.

[0053] A low-molecular-weight organic silicon compound is the hypoviscosity, and viscosity change can make the nonaqueous-solution system electrolytic solution contain it as an ion conductivity improver using the property of being small. Since the volatility of metal ions, such as a lithium ion, can be raised and the good ion conductivity can be kept stable by this, it becomes possible to obtain a cell with little temperature dependence.

[0054] Since the low-molecular-weight organic silicon compound as this ion conductivity improver not only contributes to the viscosity down of the nonaqueous-solution system electrolytic solution, but has further the operation which raises the surface activity of an electrode active material as described above, it contributes also to improvement in the plain-gauze fibers for plastering of the.

intercalation of the metal ion in the positive-electrode layer 3 and the negative-electrode layer 6, and a day intercalation. The internal impedance of a cell can be reduced and this enables it to aim at an improvement of cell efficiency.

[0055] Furthermore, as mentioned above, it excels in stability, and a low-molecular-weight organic silicon compound has little chemical change by the cell voltage, and since it is rich in degradation-proof nature, even if it uses it for a long period of time, it can obtain a quality cell with little property degradation by using the nonaqueous-solution system electrolytic solution using the low-molecular-weight organic silicon compound as one component.

[0056] Here, the non-drainage system solvent in the nonaqueous-solution system electrolytic solution is usually used as a mixed solvent which combined the solvent which has a high dielectric constant as mentioned above, and the solvent of hypoviscosity. A low-molecular-weight organic silicon compound can be blended and used for the conventional nonaqueous-solution system electrolytic solution as an ion conductivity improver, as mentioned above, and although used as some low viscosity solvents described above in this case, it is also possible to use as a subject of a low viscosity solvent further. Also in this case, a low-molecular-weight organic silicon compound cannot be overemphasized by functioning as an ion conductivity improver.

[0057] Also in any of a use gestalt of a low-molecular-weight organic silicon compound which was described above, it is desirable to use what is excellent in a low-molecular-weight organic silicon compound and compatibility for other solvents, and a solvation coefficient (SP value) a low-molecular-weight organic silicon compound specifically Since it is five to about six, a solvation coefficient (SP value) It is desirable to use the hydrocarbon system organic solvent which is four to about 13. This is for compatibility to fall, if the difference of a solvation coefficient (SP value) is not much large, and is the more desirable solvation coefficient (SP value) of a hydrocarbon system organic solvent. It is the range of 5-10. as the solvent which specifically has a high dielectric constant -- gamma-butyrolactone (gamma-BL) etc. -- moreover, a tetrahydrofuran (THF), 2-methyl tetrahydrofuran, etc. are mentioned as a hypoviscosity solvent used together That is, as the nonaqueous-solution system electrolytic solution which blended the low-molecular-weight organic silicon compound, an electrolyte, a low-molecular-weight organic silicon compound, and a solvation coefficient (SP value) It is desirable to use the nonaqueous-solution system electrolytic-solution constituent containing about (five to about [ Preferably ] 10) four to 13 hydrocarbon system organic solvent.

[0058] Loadings of the low-molecular-weight organic silicon compound in the nonaqueous-solution system electrolytic solution 3 - 95 % of the weight Considering as the range is desirable. The loadings of a low-molecular-weight organic silicon compound are 3 % of the weight. The hypoviscosity property of the low-molecular-weight organic silicon compound concerned is it hard to be demonstrated to be the following notably, and, on the other hand, it is 95 % of the weight. Since the dielectric constant of a combination solvent composition system will fully be hard to be maintained if it exceeds, it becomes less not suitable in the quality of the solvent for cells. Especially, when considering as the good solvent for cells of the balance which fully demonstrated these both special feature, they are the loadings of a low-molecular-weight organic silicon compound. 5 - 80 % of the weight Considering as the range is desirable.

[0059] the chain-like organic silicon compound to which the low-molecular-weight organic silicon compound used as one component of the nonaqueous-solution system electrolytic solution is expressed with (1) formula -- and -- Although you may be any of the annular organic silicon compound expressed with (2) formulas, a low chain-like organic silicon compound is preferably used more for viscosity. Moreover, it is 95 - 10 % of the weight about a compounding ratio [ more as opposed to / when using it as such mixture / the annular organic silicon compound of a low chain-like organic silicon compound in viscosity ]. Considering as the range is desirable and it is 90 - 50 % of the weight more preferably. It is a range.

[0060] The nonaqueous-solution system electrolytic solution which a low-molecular-weight organic

silicon compound which was mentioned above contained inevitably, or the nonaqueous-solution system electrolytic solution blended positively is preferably used for the solid-state polyelectrolyte type lithium secondary battery of the operation gestalt mentioned above, for example. The concrete composition of a lithium secondary battery is as having mentioned above, and the lithium secondary battery using the solution system electrolytic solution containing this low-molecular-weight organic silicon compound serves as an operation gestalt of the solid-state polyelectrolyte type cell of this invention.

[0061] Moreover, irrespective of the existence of intervention of a plasticizer, it can be used for the various solid-state polyelectrolyte type cells mentioned above, and also the solution system electrolytic solution containing the above-mentioned low-molecular-weight organic silicon compound can be used as the electrolytic solution of not only a solid-state polyelectrolyte type cell but various kinds of nonaqueous-solution system cells.

[0062]

[Example] Next, the concrete example of this invention is explained.

[0063] examples 1-2 and the examples 1-4 of comparison -- the example of the manufacture method of the solid-state polyelectrolyte type cell of this invention is explained first It is LiCoO<sub>2</sub> as an active material of a positive electrode. The lithium content cobalt oxide expressed (Japan Metals & Chemicals Co., Ltd. make), as the high molecular compound which holds acetylene black and the nonaqueous-solution system electrolytic solution as a conductive material, and functions as a binder (VdF-HFP) -- copolymer powder (the product made from ERUFATOKEMU --) Kynar 2801 and the copolymerization ratio of VdF:HFP prepared the dibutyl phthalate (DBP) as 88:12 and a plasticizer, and in the acetone as a solvent, it mixed and they pasted these so that it might be set to 56:5:17:22 by the weight ratio. About 150 micrometers in thickness it is thin in a positive-electrode layer by vaporizing the above-mentioned solvent after applying this paste by the knife coating machine on the aluminum mesh as a charge collector The plasticizer content stratified Plastic solid was produced.

[0064] The DBP same as the copolymer powder same (VdF-HFP) as a high molecular compound which holds a mesophase pitch based carbon fiber (Product made from PETOKA) and the nonaqueous-solution system electrolytic solution as an active material of a negative electrode, and functions as a binder on the other hand as a positive electrode, and a plasticizer as a positive electrode was prepared, in the acetone as a solvent, it mixed and these were pasted so that it might be set to 58:17:25 by the weight ratio. Thickness abbreviation which serves as a negative-electrode layer by vaporizing the above-mentioned solvent after applying this paste by the knife coating machine on the copper mesh as a charge collector 130 micrometers The plasticizer content stratified Plastic solid was produced.

[0065] Next, like the above-mentioned positive electrode and the above-mentioned negative electrode, in the acetone as a solvent, it mixed and the copolymer (VdF-HFP) as a high molecular compound and DBP as a plasticizer holding the nonaqueous-solution system electrolytic solution were pasted so that it might be set to 50:50 by the weight ratio. About 90 micrometers in thickness which exfoliates from a glass plate and serves as a base-material layer of a solid-state polyelectrolyte layer after applying this paste by the knife coating machine on a glass plate and vaporizing the above-mentioned solvent The plasticizer content stratified Plastic solid was produced.

[0066] Thus, after carrying out the laminating of the stratified Plastic solid and charge collector used as the stratified Plastic solid used as a charge collector [ used as the obtained positive electrode ] and stratified Plastic-solid, and solid-state polyelectrolyte layer, and a negative electrode in this sequence, it was stuck by pressure by the hot calender roll of 403K, and the laminated-structure object which becomes the origin of the cell cell 8 shown in drawing 1 was produced.

[0067] Next, hexa methyl disiloxane (MM) was first used for the extracting solvent of DBP as an example 1, the above-mentioned laminated-structure object was immersed in MM of ordinary temperature, dissolution extraction was carried out and DBP which is a plasticizer was removed. It is

the degree of ultraviolet-rays spectral extinction about the removal grade of DBP. 275 micrometers As a result of pursuing on wavelength, it is time until it is no longer detected. They were 5 - 8 minutes.

[0068] Moreover, octamethylcyclotetrasiloxane (D4) was used for the extracting solvent of DBP as an example 2, the laminated-structure object produced similarly was immersed in D4 of ordinary temperature, dissolution extraction was carried out and DBP which is a plasticizer was removed. As a result of pursuing the removal grade of DBP like an example 1, it is time until it is no longer detected. It was 7 - 10 minutes.

[0069] As an example of comparison with this invention, diethylether (example 1 of comparison), the methanol (example 2 of comparison), and the laminated-structure object through which it passed and that was produced similarly, using Korean geisha (example 3 of comparison) respectively were immersed in the extracting solvent of DBP at each organic solvent of ordinary temperature, dissolution extraction was carried out and DBP which is a plasticizer was removed. As a result of pursuing the removal grade of DBP like an example 1, time was 10 - 15 minutes, 17 - 25 minutes, and 30 - 40 minutes, respectively until it was no longer detected.

[0070] It turns out that MM of an example 1 and two example D4 are extremely excellent in the extraction capacity of DBP so that clearly from the above-mentioned removal result of DBP. MM and D4 have [ this ] small surface tension compared with the extracting solvent of the example of comparison -- originating -- \*\*\*\* -- the sake -- MM and D4 -- the interior of the laminated-structure object of a cell -- deep -- alike -- until -- it permeates promptly and this can remove DBP in a short time

[0071] Moreover, since an extracting solvent needed vaporizing promptly and not making it remain from a laminated-structure object after extraction of DBP is completed (however, there is nothing a between title even if it remains in the case of low-molecular-weight organic silicon compounds by this invention, such as MM), the cell laminated-structure object concerned was left in the room temperature after the removal end of DBP, and time until an extracting solvent stops remaining inside was measured. Consequently, the example 1 was [ each example of comparison of the example 2 ] 10 - 15 minutes, 50 - 70 minutes, and 120 minutes or more for 17 to 22 minutes for 15 to 20 minutes, respectively.

[0072] Thus, to the cell laminated-structure object of each example which removed DBP completely, and each example of comparison, it is a volume ratio about ethylene carbonate (EC) and dimethyl carbonate (DMC). It is one-mol LiPF<sub>6</sub> at ordinary temperature to the mixed solvent mixed by 2:1. The \*\*\*\*\* system electrolytic solution which dissolved and prepared the electrolyte was sunk in, respectively. this wet out rate is very quick -- also after that, although the amount of saturation sinking in is mostly reached in 5 minutes, in order to sink in, in this example, a few was immersed for 20 minutes and infiltrated

[0073] Thus, obtained area 4cm<sup>2</sup> About the cell cell of each example and each example of comparison, the rate of impregnation, ionic conductivity, and internal impedance of the electrolytic solution were measured. Moreover, about each cell cell into which these electrolytes were infiltrated, after charging to 4.2V by the charging current of 1C, the charge-and-discharge cycle which discharges with the current of 1C to 2.7V was repeated, and each capacity maintenance factor to the initial cell capacity of a deed, the initial cell capacity (mAh) of 1 cycle eye and 10 cycles, 50 cycle, and a 100 cycle eye was measured. These measurement results are shown in Table 1. In addition, except not using DBP in the above-mentioned example, the example 4 of comparison shown in Table 1 produces a cell cell similarly, and performs same measurement about this cell cell.

[0074]

[Table 1]

	DBP 抽出溶媒	電解液 含浸率 (wt%)	イオン 伝導度 (S/cm)	内部 インピーダンス ( $\Omega$ )	初期 容量 (mAh)	容量維持率(%)		
						10回	50回	100回
実施例1	ヘキサメチルジシロキサン	65	$4.3 \times 10^{-2}$	57	13	97	92	90
実施例2	オクタメチルシクロテトラシロキサン	68	$4.5 \times 10^{-2}$	60	12	98	95	92
比較例1	メチルセレン	58	$8.1 \times 10^{-3}$	139	9	96	93	89
比較例2	メタノール	51	$2.0 \times 10^{-3}$	205	5	91	87	81
比較例3	ヘキサン	53	$2.5 \times 10^{-3}$	188	7	92	85	77
比較例4	(DBP無添加)	37	$6.2 \times 10^{-5}$	>500	2	76	40	12

Since hexa methyl disiloxane (MM) and octamethylcyclotetrasiloxane (D4) do not shrink a high molecular compound, in an example 1 and the example 2, they can enlarge rate of impregnation of the electrolytic solution, and, therefore, are understood that ionic conductivity is good, initial cell capacity is large and a charge-and-discharge cycle property is also good, so that clearly from Table 1. Moreover, based on the reforming effect on the front face of an active material by MM or D4, for this reason, the internal impedance of a cell can fully supply cell capacity to a load, and a low excels [ internal impedance ] in the so-called cell efficiency.

[0075] In order to shrink the high molecular compound concerned at the same time it extracts DBP from a high molecular compound to these by each extracting solvent by the examples 1-3 of comparison, the amount of sinking in of the part ion electrolytic solution decreases, the initial cell capacity of a cell is low, and a charge-and-discharge cycle property is also bad. Moreover, the internal impedance of a cell is also known by that it is high compared with an example.

[0076] In addition, the result with the same said of the case where replaced with MM of the above-mentioned example 1, and octamethyl trisiloxane (MDM) and a decamethyl tetrapod siloxane (MD2M) are used was obtained, and the result with the same said of the case where replaced with the two above-mentioned example D4, and decamethyl cyclopentasiloxane (D5) is used was obtained.

[0077] Examples 3-4, the example 5 of comparison, next the example of the solid-state polyelectrolyte type cell of this invention are explained.

[0078] The mixed weight ratio of this, methylethyl carbonate (MEC), and gamma-butyrolactone, using hexa methyl disiloxane (MM) as a low-molecular-weight organic silicon compound About the partially aromatic solvent (solvation coefficient (SP value) =9.5) of 1:1, the compounding ratio of MM is 30 % of the weight to the above-mentioned partially aromatic solvent. It mixes so that it may become, and it is in ordinary temperature to this mixed solvent. One-mol LiPF<sub>6</sub> The electrolyte was dissolved and the nonaqueous-solution system electrolytic solution (example 3) was prepared.

[0079] Moreover, octamethylcyclotetrasiloxane (D4) is used as a low-molecular-weight organic silicon compound, and, for the weight ratio of this, dimethyl carbonate, and a sulfolane, the compounding ratio of D4 is 45 % of the weight about the liquid (solvation coefficient (SP value) =10.2) of 2:1. It mixes so that it may become, and it is in ordinary temperature to this mixed solvent. Two mols LiBF<sub>4</sub> The electrolyte was dissolved and the nonaqueous-solution system electrolytic solution (example 4) was prepared.

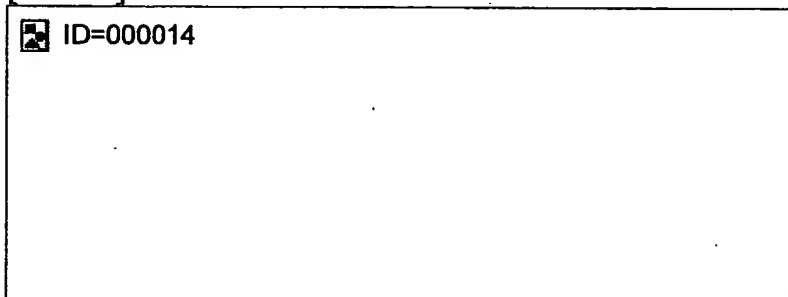
[0080] Furthermore, it is a weight ratio about methylethyl carbonate (MEC) and gamma-butyrolactone as an example 5 of comparison. It mixes so that it may be set to 1:1, and it is in ordinary temperature to this mixed solvent. One mol LiPF<sub>6</sub> The electrolyte was dissolved and the nonaqueous-solution system electrolytic solution was prepared.

[0081] It sank into the cell laminated-structure object which produced each nonaqueous-solution system electrolytic solution by each examples 3 and 4 and the example 5 of comparison which were

mentioned above like the above-mentioned examples 1 and 2 and the example 1 of comparison, respectively (sinking-in time =20 minute).

[0082] Thus, obtained area 4cm<sup>2</sup> About the cell cell of each example and each example of comparison, the rate of impregnation, ionic conductivity, and internal impedance of the electrolytic solution were measured. Moreover, about each cell cell into which these electrolytes were infiltrated, after charging to 4.2V by the charging current of 1C, the charge-and-discharge cycle which discharges with the current of 1C to 2.7V was repeated, and each capacity maintenance factor to the initial cell capacity of a deed, the initial cell capacity (mAh) of 1 cycle eye and 10 cycles, 50 cycle, and a 100 cycle eye was measured. These measurement results are shown in Table 2.

[Table 2]



It turns out that the cell using the nonaqueous-solution system electrolytic solution which blended hexa methyl disiloxane (MM) and octamethylcyclotetrasiloxane (D4) is excellent in each of ionic conductivity, internal impedance, initial cell capacity, and charge-and-discharge cycle properties so that clearly from Table 2. Especially, in the example 3 and the example 4, since ionic conductivity improved by leaps and bounds, even if it performed the charge and discharge of 2-3C, the flattery nature of movement between poles of electrolyte ion was good, and, thereby, broadening was shown in the correspondence to the big load of boosting charge and service capacity.

[0083]

[Effect of the Invention] As explained above, while being able to raise the amount of sinking in of the extraction efficiency of a plasticizer, etc. and the nonaqueous-solution system electrolytic solution according to the manufacture method of the solid-state polyelectrolyte type cell of this invention, even if an extracting solvent remains in a solid-state polyelectrolyte layer, it does not have a bad influence on a fuel cell subsystem. It becomes possible to be stabilized and to obtain the solid-state polyelectrolyte type cell excellent in ion conductivity, internal impedance, the charge-and-discharge cycle property, etc. by these. Moreover, according to the nonaqueous-solution system electrolytic solution for cells of this invention, it becomes possible to aim at reduction in viscosity, improvement in the surface activity of an electrode active material, etc. further.

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**TECHNICAL FIELD**

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[The technical field to which invention belongs] this invention relates to the nonaqueous-solution system electrolytic solution for cells used for the manufacture method of a solid-state polyelectrolyte type cell of having used the nonaqueous-solution system electrolytic solution, a solid-state polyelectrolyte type cell, and a nonaqueous-solution system cell.

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## PRIOR ART

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[Description of the Prior Art] It is indispensable to the electrolytic solution of the lithium cell which dislikes water in order to react violently with moisture from a standpoint with practical using the nonaqueous-solution system electrolytic solution, and such a lithium secondary battery is well known as a nonaqueous-solution system cell. Since the cell energy density is large, such a lithium secondary battery has been multiple-use-ized as a power supply of the cordless device which thinks small lightweight nature as important etc. Moreover, this cell function Development of the lithium ion solid-state polyelectrolyte type rechargeable battery provided as an about 0.5mm single cell of a super-thin shape (LPB), i.e., the cell using the organic high molecular compound which has the maintenance function of the nonaqueous-solution system electrolytic solution as a solid electrolyte layer, is also performed actively, and utilization level is reached. Although improvement of many component engineerings, such as selection, cell construction, etc. of the active material of a positive electrode and a negative electrode, has contributed to utilization of these rechargeable batteries, selection of the electrolytic solution is expected much more improvement in technical.

[0003] Here, the strong-base solution of a potassium hydroxide is used for the electrolytic solution of a solution system cell. the liquid property that the operation effect of the electrolytic solution over a cell reaction here is the hypoviscosity of water, and is large, and the good ionic conduction nature of about 10 to 2 or more ohm/cm by the potassium hydroxide as solution have realized exertion of a practical cell capacity required for a cell, and correspondence to a big load [ of specific inductive capacity ] On the other hand, by the nonaqueous-solution system cell, the present condition is racking one's brains for maintaining big ionic conduction nature compared with the solution system electrolytic solution stably, by the use potential difference of a cell, since there are few liquids with low viscosity (solvent). It is 50 % of the weight about the ion electrolyte content in the solid-state polyelectrolyte layer especially used in a LPB type. If it is not made a grade above, also theoretically and experimentally, it is checked that a fully practical cell is not obtained.

[0004] In order to raise the content of the electrolyte in a solid-state polyelectrolyte layer, some methods are tried from the former. The technology As one, the method using the high molecular compound which includes hetero atom teams, such as alkylene oxide, in the molecular structure as a solid-state polyelectrolyte layer is mentioned (refer to Japanese Patent Publication No. 6 No. -52671 official report). Such a solid-state polyelectrolyte layer is 50 % of the weight about an electrolyte. It is known that it is possible to make it sink in above. However, since the hetero atom team which sank in the electrolyte becomes a sea phase in the macromolecule structure which constitutes a solid-state polyelectrolyte layer and the macromolecule principal chain except a hetero atom team forms the discontinuous phase, the fluidity of a discontinuous phase will increase an electrolyte, so that it high-sinks in. That is, the present condition is being unable to make [ many / that the electrolytic amount of sinking in is expected in order to present long-term use with an electrolyte as a practical cell from a bird clapper as a configuration is unstable so that it high-sinks in / so ] it.

[0005] As other methods, it is for example, the U.S. \*\*\*\*\*. There is technology which sinks an electrolyte into this amorphous phase using the high molecular compound with which the crystal phase and the amorphous phase were intermingled as a solid-state polyelectrolyte layer as indicated by No. 5,456,000. although the instability of configuration maintenance which is seen in the solid-state polyelectrolyte layer which has the hetero atom team of the above-mentioned [ this technology ] is avoidable practically -- electrolytic rate of impregnation -- at most 30 - 40 % of the weight Since it



is a grade, like  $10^{-5}$  -  $10^{-4}$  ohm/cm, only a degree is obtained but it passes over ionic conductivity low as a practical use cell.

[0006] For this reason, the above-mentioned U.S. \*\*\*\*\* In No. 5,456,000 A film is produced using the raw material which blended a plasticizer like a dibutyl phthalate, dimethyl phthalate, and tris-butoxy ethyl phosphate with polymeric materials like the fluoride vinylidene-hexafluoropropylene copolymer (it is hereafter described as a copolymer (VdF-HFP)) used as a polyelectrolyte, and blended this plasticizer with them, and a lower alcohol like ethanol, diethylether, a tetrahydrofuran, and the technology that sinks in the nonaqueous-solution system electrolytic solution containing an electrolyte after passing and carrying out extraction removal with a low boiler like Korean geisha are indicated in the plasticizer out of this film. By applying such a method, it is 60 - 70 % of the weight about the rate of impregnation of the nonaqueous-solution system electrolytic solution. It can carry out and it is shown that ionic conductivity improves to  $10^{-2}$  -  $10^{-3}$  ohm/cm.

[0007] When adopting the above-mentioned method, it is necessary to remove a plasticizer completely by the fuel cell subsystem in order to start an oxidation-reduction reaction with the operating potential of a cell. However, it had the problem that the conventional extracting solvent which was mentioned above has the solubility of a plasticizer, and the inadequate diffusion permeability inside a high molecular compound, and full extraction of a plasticizer takes it for a long time, and a problem which is referred to as having a bad influence on a fuel cell subsystem in response to oxidation reduction by the cell busy condition when an extracting solvent remains in a solid-state polyelectrolyte layer again. Furthermore, while each conventional extracting solvent mentioned above carried out dissolution extraction of the plasticizer, it shrank the high molecular compound used as a solid-state polyelectrolyte layer, and it had the fault of reducing the amount of sinking in of the nonaqueous-solution system electrolytic solution. Moreover, when the work environment of the dissolution extraction process of a plasticizer etc. is taken into consideration, an extracting solvent is wanted to have the property of not checking earth environment as it is safe to a human body and is observed further recently.

[0008] On the other hand, an improvement aiming at much more improvement in charge-and-discharge efficiency etc. is desired about the nonaqueous-solution system electrolytic solution itself. That is, the nonaqueous-solution system electrolytic solution consists of ionicity compounds (electrolyte) which are dissolved in an organic solvent and it and perform ionic migration in it. Among these, in addition to being a high dielectric constant, an organic solvent is asked for it being the low viscosity which makes ionic conduction easy in the operation temperature of a cell so that internal impedance of a cell may not be raised. Although high dielectric constant matter, such as ethylene carbonate, is used for the solvent of the conventional nonaqueous-solution system electrolytic solution, it is a solid-state, and the electrolytic solution actual since there are many liquids with high viscosity is mixed with the solvent of hypoviscosity, apparent electrolytic-solution viscosity is made low, and it is made not to spoil the mobility of a metal ion in ordinary temperature. Moreover, the solvent of hypoviscosity is expected to be the liquid which may raise the surface activity of an active material to an electrode active material layer in order to make metal ions, such as a lithium ion, easy to intercalate or deintercalate.

[0009] As a solvent of hypoviscosity with which a property which was mentioned above is demanded, although chain-like carbonate, such as dimethyl carbonate and JIEME chill carbonate, etc. is used conventionally, when aiming at improvement in a cell property, the solvent which can raise the surface activity of much more reduction in the viscosity of the nonaqueous-solution system electrolytic solution or an electrode active material is called for.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] As explained above, while being able to raise the amount of sinking in of the extraction efficiency of a plasticizer, etc. and the nonaqueous-solution system electrolytic solution according to the manufacture method of the solid-state polyelectrolyte type cell of this invention, even if an extracting solvent remains in a solid-state polyelectrolyte layer, it does not have a bad influence on a fuel cell subsystem. It becomes possible to be stabilized and to obtain the solid-state polyelectrolyte type cell excellent in ion conductivity, internal impedance, the charge-and-discharge cycle property, etc. by these. Moreover, according to the nonaqueous-solution system electrolytic solution for cells of this invention, it becomes possible to aim at reduction in viscosity, improvement in the surface activity of an electrode active material, etc. further.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] As mentioned above, in the manufacturing process of the solid-state polyelectrolyte layer of the nonaqueous-solution system cell which used the conventional plasticizer together, the extracting solvent of a plasticizer which has a property as shown below is called for. That is, even if the vapor pressure in the extraction temperature which does not shrink a high molecular compound at the time of the extraction of a plasticizer which carries out diffusion osmosis promptly to the interior of the high molecular compound which solubility with a plasticizer is large, and surface tension is small, and constitutes a solid-state polyelectrolyte layer should vaporize promptly greatly and should further remain in a high-molecular-compound layer, while it is safe for the human body which does not have a bad influence on a fuel cell subsystem, an extracting solvent of a plasticizer which does not check earth environment and which has the property of \*\* is desired

[0011] Moreover, about the nonaqueous-solution system electrolytic solution itself, while an improvement aiming at improvement in charge-and-discharge efficiency etc. is desired and specifically being able to form the nonaqueous-solution system electrolytic solution into low viscosity further, the solvent which can raise the surface activity of an electrode active material is called for.

[0012] In case this invention was made in order to cope with such a technical problem, uses a plasticizer together and manufactures the solid-state polyelectrolyte type cell using the nonaqueous-solution system electrolytic solution, while it raises the amount of sinking in of the extraction efficiency of a plasticizer, etc. and the nonaqueous-solution system electrolytic solution. It aims at offering the manufacture method of a solid-state polyelectrolyte type cell and solid-state polyelectrolyte type cell which do not have a bad influence on a fuel cell subsystem even if an extracting solvent should remain in a solid-state polyelectrolyte layer. It aims at offering the nonaqueous-solution system electrolytic solution for cells which furthermore aimed at reduction in viscosity, and improvement in the surface activity of an electrode active material further.

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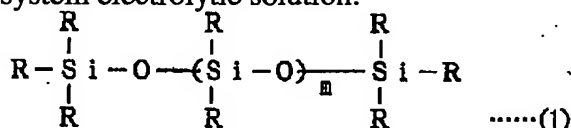
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**MEANS**


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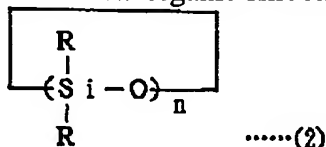
[Means for Solving the Problem] The result which advanced examination about various solvents in order to attain the above-mentioned purpose, the low-molecular-weight chain-like organic silicon compound expressed with the following (1) formula -- and -- The low-molecular-weight annular organic silicon compound expressed with (2) formulas Are the right solution of the plasticizer used for (a) cell formation, dissolve almost all plasticizers easily and carry out extraction removal. Even if (b) surface tension compares with the conventional extraction solution 15 dyn/cm order, are small. It is easy to permeate the detailed portion of a cell composition constituent quickly. Do not shrink a high molecular compound at the time of extraction of the (c) plasticizer. (d) The vapor pressure in extraction temperature vaporizes promptly greatly. Earth environment is not spoiled while it is very safe for the (e) human body. It has the various properties for which the extracting solvent of the plasticizer at the time of using a plasticizer together and manufacturing a solid-state polyelectrolyte layer is asked, and adds to it. (f) While being essentially hypoviscosity The viscosity change in the temperature requirement of a cell busy condition is small, is stabilized in the volatility of a metal ion, and can raise. There was little change chemical under (g) cell service condition, and while not having a bad influence on a fuel cell subsystem, it found out having various properties for which the hypoviscosity solvent of the nonaqueous-solution system electrolytic solution is asked, such as being rich in degradation-proof nature.

[0014] It is [Formula 7] about the aforementioned plasticizer as the manufacture method of the solid-state polyelectrolyte type cell of this invention was indicated to the claim 1, after having accomplished this invention based on knowledge which was described above, and fabricating the macromolecule constituent containing a plasticizer and the aforementioned high molecular compound in layers in the manufacture method of a solid-state polyelectrolyte type cell that opposite arrangement of a positive electrode and the negative electrode was carried out, through the solid-state polyelectrolyte layer which has a high-molecular-compound layer holding the nonaqueous-solution system electrolytic solution.



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは0～7の整数を示す)

The chain-like organic silicon compound come out of and expressed, and [Formula 8]



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは3～10の整数を示す)

It is coming out and being chosen out of the annular organic silicon compound expressed that it is

few. It is characterized by having the process which carries out dissolution extraction using one sort of low-molecular-weight organic silicon compounds, and the process which sinks the aforementioned nonaqueous-solution system electrolytic solution into the aforementioned high-molecular-compound layer by which dissolution extraction of the aforementioned plasticizer was carried out, and forms the aforementioned solid-state polyelectrolyte layer.

[0015] Moreover, the solid-state polyelectrolyte layer which has the high-molecular-compound layer in which the solid-state polyelectrolyte type cell of this invention held the nonaqueous-solution system electrolytic solution, In the solid-state polyelectrolyte type cell possessing the positive electrode and negative electrode by which opposite arrangement was carried out through the aforementioned solid-state polyelectrolyte layer the aforementioned nonaqueous-solution system electrolytic solution the above The chain-like organic silicon compound expressed with (1) formula, and the above it is chosen out of the annular organic silicon compound expressed with (2) formulas -- at least -- One sort of low-molecular-weight organic silicon compounds It is characterized by the bird clapper from the nonaqueous-solution system electrolytic-solution constituent contained as an ion conductivity improver.

[0016] furthermore, the nonaqueous-solution system electrolytic solution for cells of this invention -- the above The chain-like organic silicon compound expressed with (1) formula, and the above it is chosen out of the annular organic silicon compound expressed with (2) formulas -- at least -- It is characterized by the bird clapper from the nonaqueous-solution system electrolytic-solution constituent which contains one sort of low-molecular-weight organic silicon compounds as an ion conductivity improver.

[0017]

[Embodiments of the Invention] Hereafter, the form for carrying out this invention is explained.

[0018] 1 operation form which applied the manufacture method of the solid-state polyelectrolyte type cell of this invention to the manufacture method of the lithium secondary battery of a nonaqueous-solution system is explained. Before explaining the manufacture method in full detail, the composition of the rechargeable battery of a nonaqueous-solution system lithium is first explained with reference to drawing 1 . In addition, this lithium secondary battery is 1 operation form of the solid-state polyelectrolyte type cell of this invention, and this invention is not limited to this.

[0019] Drawing 1 shows, solid-state polyelectrolyte type the important section, i.e., the cell cell portion, of a lithium secondary battery of this operation gestalt, and 1 is the positive electrode which carried out laminating formation and constituted the positive-electrode layer 3 on the charge collector 2. Moreover, 4 is the negative electrode which carried out laminating formation and constituted the negative-electrode layer 6 on the charge collector 5, and it is arranged so that the negative-electrode layer 6 of this negative electrode 4 may counter with the positive-electrode layer 3 of a positive electrode 1. Between these positive electrodes 1 and the negative electrode 4, it intervenes so that the solid-state polyelectrolyte layer 7 may be located between the positive-electrode layer 3 and the negative-electrode layer 6. The cell cell 8 is constituted by these and a solid-state polyelectrolyte type lithium secondary battery is constituted by holding a winding object, a layered product, etc. of this cell cell 8 in a cell container.

[0020] The above-mentioned positive electrode 1 has the structure which supported with the charge collector 2 the positive-electrode layer 3 as a barrier layer which consists of high molecular compounds holding an active material, the nonaqueous-solution system electrolytic solution, and this electrolytic solution. here -- the various oxides  $2O_4$  as an active material, for example,  $LiMn$ , etc. -- a lithium manganese multiple oxide and  $LiNiO_2$  etc. -- a lithium content nickel oxide and  $LiCoO_2$  etc. -- cull GEKON compounds containing a lithium content cobalt oxide, a lithium content nickel cobalt oxide, and a lithium, such as for example, an amorphous vanadium pentoxide, etc. 2 titanium sulfides, and molybdenum disulfide, etc. can be mentioned Especially, a lithium manganese multiple oxide, a lithium content cobalt oxide, and a lithium content nickel oxide are preferably used for a top with little degradation by electric field from the efficiency of the charge which can be used as a cell being good.

[0021] The nonaqueous-solution system electrolytic solution mentioned above is adjusted by dissolving an electrolyte in non-drainage system solvents, such as an organic solvent. As a non-

drainage system solvent, ethylene carbonate (EC), propylene carbonate (PC), Butylene carbonate (BC), dimethyl carbonate (DMC), Diethyl carbonate (DEC), ethyl methyl carbonate (EMC), gamma - A butyrolactone (gamma-BL), a sulfolane, an acetonitrile, 1, 2-dimethoxyethane, 1, 3-dimethoxypropane, a wood ether, organic solvents generally used as the electrolytic solution for cells, such as a tetrahydrofuran (THF) and 2-methyl tetrahydrofuran, -- in addition, it mentioned above (1) formula -- or -- The low-molecular-weight organic silicon compound expressed with (2) formulas can be mentioned.

[0022] Usually, a non-drainage system solvent is used as a mixed solvent which combined the solvent which has a high dielectric constant, and the solvent of hypoviscosity, and a low-molecular-weight organic silicon compound can be used as a kind of a low viscosity solvent etc. In addition, the low-molecular-weight organic silicon compound used as a kind of this low viscosity solvent etc. and the nonaqueous-solution system electrolytic-solution constituent using this are explained in full detail behind.

[0023] Moreover, as the above-mentioned electrolyte, the lithium salt of a lithium perchlorate ( $\text{LiClO}_4$ ), a 6 fluoride [ phosphoric-acid ] lithium ( $\text{LiPF}_6$ ), hoe 4 lithium fluoride ( $\text{LiBF}_4$ ), a 6 fluoride arsenic lithium ( $\text{LiAsF}_6$ ), a trifluoromethane sulfonic-acid lithium ( $\text{LiCF}_3\text{SO}_3$ ), a screw trifluoromethyl SURUHOMECHIRUHONIRUIMIDO lithium [ $\text{LiN}(\text{CF}_3\text{SO}_3)_2$ ], etc. is mentioned, for example. The amount of dissolutions to the non-drainage system solvent of these electrolytes It is desirable to consider as about 0.2-2 mol/L.

[0024] An alkylene-oxide system high molecular compound like fluorine system high molecular compounds, such as a fluoride vinylidene and fluoride vinylidene-hexafluoropropylene copolymer (VdF-HFP) (copolymer), and a polyethylene oxide as a high molecular compound holding the nonaqueous-solution system electrolytic solution which was mentioned above etc. can be mentioned. In this case, it does not use independently as a binder of an active material, and (VdF-HFP) does not bar mixing with a copolymer and using polyvinylidene fluoride and a fluorine system high molecular compound like a polytetrafluoroethylene.

[0025] When producing by the same method as the solid-state polyelectrolyte layer 7 which mentions the positive-electrode layer 3 as a barrier layer later among the above-mentioned high molecular compounds, it is desirable to use a fluoride vinylidene and a copolymer (VdF-HFP). In addition, in order to give conductivity to the positive-electrode layer 3, carbon black, such as an artificial graphite and acetylene black, nickel powder, etc. can be used together.

[0026] Moreover, as a charge collector 2 of a positive electrode 1, the foil of aluminum or nickel, a mesh, an expanded metal, punched metal, etc. are used, for example.

[0027] The negative electrode 4 has the structure which supported with the charge collector 5 the negative-electrode layer 6 as an active material layer which consisted of high molecular compounds holding an active material, the nonaqueous-solution system electrolytic solution, and this electrolytic solution etc., and it is arranged through the solid-state polyelectrolyte layer 7 so that the negative-electrode layer 6 may counter with the positive-electrode layer 3 of a positive electrode 1. Although the basic structure of a negative electrode 4 and a part of material of construction are similar with the positive electrode 1 mentioned above, a positive electrode 1 and the material in which it differs are the active material which intercalates a lithium ion, and the quality of the material of a charge collector 5.

[0028] That is, in a lithium ion, it is possible occlusion and to emit, namely, to intercalate and deintercalate to the active material which is one of the components of the negative-electrode layer 6, for example, carbonaceous material is used for it. The carbonaceous material represented by what calcinates organic high molecular compounds, such as phenol resin, a polyacrylonitrile, and a cellulose, for example, and obtained as this carbonaceous material, the thing which calcinates corks and a pitch and is obtained, artificial graphite, natural graphite, etc. can be mentioned. Especially, it is under an ordinary pressure or reduced pressure in inert gas atmosphere, such as an argon and nitrogen. It is known that the mezzo-soprano carbon which calcinates the above-mentioned organic high molecular compound, and is obtained at the temperature of 773-3273K is excellent in the intercalation property of a lithium ion. In order to aim at conductive improvement, of course, you may use KETCHIEN black, carbon black, etc. together.

[0029] Moreover, as a charge collector 5 of a negative electrode 4, it replaces with the aluminum in a positive electrode 1 etc., and the thing of the appearance configuration of the positive-electrode charge collector 2 and the same configuration is used using copper etc. In addition, the same thing as the positive-electrode layer 3 is used for the high molecular compound which is one of the components of the negative-electrode layer 6. Moreover, it is as having mentioned above about the nonaqueous-solution system electrolytic solution.

[0030] The solid-state polyelectrolyte layer 7 arranged between the positive electrodes 1 and negative electrodes 4 which were mentioned above consists of high molecular compounds holding the nonaqueous-solution system electrolytic solution which was mentioned above, and this electrolytic solution. That is, the solid-state polyelectrolyte layer 7 is constituted by making the nonaqueous-solution system electrolytic solution sink in and hold in the high-molecular-compound layer which has the maintenance function of the nonaqueous-solution system electrolytic solution. in this invention, when forming a high-molecular-compound layer so that it may explain in full detail behind, the plasticizer was used together, and this plasticizer was mentioned above (1) formula -- or -  
- The nonaqueous-solution system electrolytic solution is high-infiltrated into a high-molecular-compound layer by carrying out extraction removal by the low-molecular-weight organic silicon compound expressed with (2) formulas.

[0031] As a high molecular compound used as the subject of the solid-state polyelectrolyte layer 7, fluorine system high molecular compounds, such as a fluoride vinylidene and a copolymer (VdF-HFP), are used, and the copolymer which is excellent in the maintenance function of the nonaqueous-solution system electrolytic solution especially mentioned above (VdF-HFP) is used preferably. In this (VdF-HFP) copolymer, especially a fluoride vinylidene contributes to improvement in a mechanical strength in the frame section of a copolymer, and hexafluoropropylene is incorporated in the state amorphous to a copolymer, and it functions as maintenance of the nonaqueous-solution system electrolytic solution, and the transparency section of a lithium ion. It is as having mentioned above about the nonaqueous-solution system electrolytic solution which sinks into the base-material layer of the solid-state polyelectrolyte layer 7 which consists of such a high molecular compound.

[0032] Next, the manufacture method of the solid-state polyelectrolyte type lithium secondary battery mentioned above is explained.

[0033] First, the production method of the solid-state polyelectrolyte layer 7 which is one of the features of this invention is described. That is, a plasticizer (plasticity solvent) is blended with fluorine system high molecular compounds mentioned above, such as a fluoride vinylidene and a copolymer (VdF-HFP), and the macromolecule constituent used as the formation material of a high-molecular-compound layer is prepared.

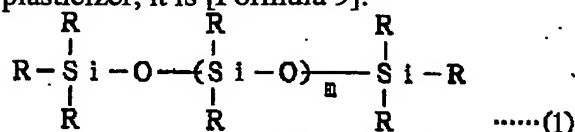
[0034] Here, as the above-mentioned plasticizer, a dibutyl phthalate (DBP), dimethyl phthalate (DMP), diethyl phthalate (DEP), propylene carbonate (PC), tris-butoxy ethyl phosphate, etc. are used. Moreover, it sets to the above-mentioned macromolecule constituent, and the loadings of these plasticizers are 20 - 70 % of the weight. Considering as the range is desirable. The loadings of a plasticizer are 20 % of the weight. There is a possibility that the amount of maintenance of the nonaqueous-solution system electrolytic solution may be insufficient in it being the following, and sufficient ion conductivity may not be obtained, and, on the other hand, the loadings of a plasticizer are 70 % of the weight. If it exceeds, configuration maintenance ability, intensity, etc. of a high-molecular-compound layer used as the base-material layer of the solid-state polyelectrolyte layer 7 will fall. It is 50 - 70 % of the weight about the loadings of a plasticizer since the dissolution extraction efficiency of a plasticizer uses a high low-molecular-weight organic silicon compound so that it may mention later in this invention especially. Even if it makes it the range and a large quantity, generating of a plasticizer residue can be prevented effectively. That is, the nonaqueous-solution system electrolytic solution can be high-infiltrated into a high-molecular-compound layer.

[0035] It is made to dissolve in an organic solvent, the macromolecule constituent containing a high molecular compound which was described above, and a plasticizer is pasted, and this macromolecule constituent paste is fabricated in layers. Specifically, after producing a macromolecule constituent paste for example, by the knife coating machine, an organic solvent is vaporized and the stratified Plastic solid of a macromolecule constituent is produced. This stratified Plastic solid may be formed



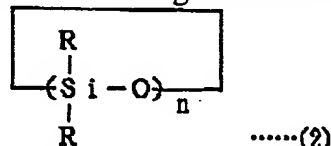
independently, and may be produced as a layered product with a positive electrode 1 or a negative electrode 4.

[0036] Next, dissolution extraction of the plasticizer contained in the stratified Plastic solid of the above-mentioned macromolecule constituent is carried out. In dissolution extraction of this plasticizer, it is [Formula 9].



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、mは0～7の整数を示す)

The chain-like organic silicon compound come out of and expressed, and [Formula 10]



(式中、Rは同一または相異なる非置換または置換の1価の有機基を、nは3～10の整数を示す)

It is coming out and being chosen out of the annular organic silicon compound expressed that it is few. One sort of liquefied low-molecular-weight organic silicon compounds are used.

[0037] the above (1) formula -- and -- As R group in (2) formulas Alkyl groups, such as a methyl group, an ethyl group, a propyl group, a butyl, and an octyl machine, Alkenyl machines, such as aryl groups, such as a phenyl group and a tolyl group, a vinyl group, and an allyl group, beta - A phenylethyl machine, gamma - Unsubstituted [ of aralkyl machines, such as a phenylpropyl machine, etc. ] A univalent organic machine, And the hydrogen atom combined with the carbon atom of these bases was replaced by a halogen atom, a cyano group, a hydroxyl group, the carboxyl group, the carbonyl group, the amino group, the alkoxy group, etc. A univalent organic machine is illustrated. Especially, a methyl group and a phenyl group are preferably used from points, such as stability, and a methyl group is especially desirable from points, such as volatility.

[0038] Moreover, it mentioned above. m in (1) formula It is the integer of 0-7. n in (2) formulas is the integer of 3-10. If the range which m and n described above is exceeded, viscosity, volatility, stability, etc. will fall. when hypoviscosity, good stability, etc. obtain especially m and n -- m considering as the range of 0-5 -- moreover, n It is desirable to consider as the range of 3-7. As the above-mentioned example of a low-molecular-weight organic silicon compound Hexa methyl disiloxane (MM), octamethyl trisiloxane (MDM), Chain-like poly methyl siloxanes, such as a decamethyl tetrapod siloxane (MD2M) Annular poly methyl siloxanes, such as octamethylcyclotetrasiloxane (D4) and decamethyl cyclopentasiloxane (D5), The compound which furthermore denaturalized all these all [ a part or ] with other alkyl groups, a phenyl group, an aralkyl machine, an alkoxy group, an ester machine, the amino group, the epoxy group, the halogenation machine, etc. is mentioned.

[0039] Extraction of the plasticizer by low-molecular-weight organic silicon compound which was mentioned above can \*\*\*\* the stratified Plastic solid of the macromolecule constituent containing a plasticizer to a low-molecular-weight organic silicon compound (liquid), or can be carried out by various methods, such as exposing the stratified Plastic solid of the macromolecule constituent which contains a plasticizer in the steam bath of a low-molecular-weight organic silicon compound. Moreover, in case it \*\*\*\* to a low-molecular-weight organic silicon compound, warming, rocking, ultrasonic irradiation, etc. can also be used together.

[0040] the interior of the stratified Plastic solid of that various plasticizers may be dissolved in the extracting solvent of a plasticizer which was mentioned above good here, and a macromolecule constituent -- deep -- alike -- until -- that it permeates promptly and a plasticizer may be dissolved efficiently, vaporizing promptly after dissolution extraction of a plasticizer and not remaining, etc. are



called for In addition, it is the property currently searched for in order for the prompt vaporization after dissolution extraction of a plasticizer to receive oxidation reduction by the cell voltage if the conventional plasticizer extracting solvent remains, and to have a bad influence on a cell property. [0041] To the demand property to such a plasticizer extracting solvent, the feature with which it is [ on the physical properties of the low-molecular-weight organic silicon compound mentioned above ] common is the right solution of a plasticizer which was first described above to the 1st, therefore can dissolve almost all plasticizers easily, and can carry out extraction removal of this efficiently.

[0042] Even if surface tension compares [ 2nd ] with the conventional extracting solvent 15 dyn/cm order, it is small, and the interior, a detailed portion, etc. of a stratified Plastic solid of a macromolecule constituent are permeated quickly, and extraction removal of the plasticizer can be carried out in a short time. In case the solid-state polyelectrolyte layer 7 is especially processed and produced as a layered product with a positive electrode 1 or a negative electrode 4, the good permeability of a low-molecular-weight organic silicon compound demonstrates an effect further.

[0043] Since it excels in volatility, after dissolution extraction of a plasticizer, it vaporizes promptly, and the extraction process of a plasticizer can be carried [ 3rd ] out efficiently. However, since it does not have a possibility of having a bad influence on a cell property even if the low-molecular-weight organic silicon compound mentioned above remains in the solid-state polyelectrolyte layer 7 and it not only does not do a bad influence, but contributes to low viscosity-ization of the nonaqueous-solution system electrolytic solution, i.e., the improvement in ionic conductivity, so that it may explain in full detail behind, improvement in a cell property can be aimed at.

[0044] Furthermore, in case the low-molecular-weight organic silicon compound which was mentioned above in addition to the feature which was described above carries out dissolution extraction of the plasticizer from the stratified Plastic solid of a macromolecule constituent, it does not almost shrink the high molecular compound used as the base material of the solid-state polyelectrolyte layer 7. This enables it to sink in more nonaqueous-solution system electrolytic solutions. This contributes to the improvement of ionic conductivity. Moreover, to a human body, environment, etc., since it is very safe, the low-molecular-weight organic silicon compound mentioned above also has the advantage of not spoiling the fabrication operation environment and the earth environment of a cell.

[0045] it mentioned above -- as -- dissolution extraction of the plasticizer from the stratified Plastic solid of a macromolecule constituent (1) formula -- or -- By using the low-molecular-weight organic silicon compound expressed with (2) formulas, it becomes possible to carry out extraction removal of the plasticizer efficiently for a short time, without making a plasticizer remain. Moreover, the low-molecular-weight organic silicon compound used for dissolution extraction will not have a bad influence on a cell property, even if it vaporizes for a short time and a low-molecular-weight organic silicon compound remains. Furthermore, in order not to almost shrink a high molecular compound, it becomes possible to infiltrate more nonaqueous-solution system electrolytic solutions.

[0046] The high-molecular-compound layer which carried out dissolution extraction of the plasticizer by the low-molecular-weight organic silicon compound turns into a base-material layer of the solid-state polyelectrolyte layer 7. And the solid-state polyelectrolyte layer 7 is obtained by infiltrating the nonaqueous-solution system electrolytic solution into this high-molecular-compound layer. The amount of sinking in of the nonaqueous-solution system electrolytic solution to a high-molecular-compound layer is 20 - 70 % of the weight, as mentioned above. The range, especially 50 - 70 % of the weight Considering as the range is desirable.

[0047] Next, the production method of a positive electrode 1 and a negative electrode 4 is described. In production of a positive electrode 1, the above-mentioned high molecular compound mixes a conductive material to a meltable organic solvent the active material first mentioned above, the high molecular compound holding the nonaqueous-solution system electrolytic solution, and if needed, and a paste is adjusted. Subsequently, the non-sunk in electrolytic-solution positive-electrode layer 3 is obtained by producing this paste. The laminating of this is carried out to a charge collector 1, and a positive electrode 1 is obtained by infiltrating the nonaqueous-solution system electrolytic solution into this. Or the above-mentioned paste can be applied to a charge collector 2, and the nonaqueous-

solution system electrolytic solution can be infiltrated into this. After producing a layered product with the solid-state polyelectrolyte layer 7, you may carry out sinking [ of the nonaqueous-solution system electrolytic solution ] in. In addition, the negative electrode 4 as well as a positive electrode 1 is produced fundamentally.

[0048] Here, you may produce the positive-electrode layer 3 and the negative-electrode layer 6 which are an active material layer through the process which carries out dissolution extraction by the low-molecular-weight organic silicon compound which mentioned the plasticizer above while using the macromolecule constituent which blended the plasticizer like the solid-state polyelectrolyte layer 7 mentioned above. That is, you may form the positive-electrode layer 3 and the negative-electrode layer 6 by carrying out dissolution extraction of the plasticizer by the low-molecular-weight organic silicon compound mentioned above from this film (layer)-like Plastic solid after pasting the active material, the high molecular compound used as the base-material layer of the positive-electrode layer 3 or the negative-electrode layer 6, and the macromolecule constituent containing a plasticizer using the organic solvent and producing this paste, and infiltrating the nonaqueous-solution system electrolytic solution after that.

[0049] Since the amount of sinking in of the nonaqueous-solution system electrolytic solution to the positive-electrode layer 3 or the negative-electrode layer 6 can be raised by applying the manufacture method which was mentioned above, improvement in a cell property can be aimed at further.

Furthermore, since the low-molecular-weight organic silicon compound mentioned above raises the surface activity of the active material contained in this stratified Plastic solid in case it carries out dissolution extraction of the plasticizer from the stratified Plastic solid of a macromolecule constituent, about a lithium ion, it intercalates, or is easy to deintercalate and it becomes an active material layer. By this, it can raise fully supplying cell capacity to a load from a bird clapper as it is possible to reduce the internal impedance of a cell, i.e., the so-called cell efficiency.

[0050] In the operation form mentioned above, although the manufacture method of this invention was explained about the case where a solid-state polyelectrolyte type lithium secondary battery is manufactured, this invention is not restricted to this, and if it is an ionic conduction type solid-state polyelectrolyte type cell, it is applicable to manufacture of various cells. Specifically, they are (-) Li/LiAlCl<sub>4</sub>-SOCl<sub>2</sub> / SOCl<sub>2</sub>. The thionyl chloride lithium cell shown by (+) etc., and (-) Li/MnO<sub>2</sub> It is possible to apply to manufacture of the lithium button cell (small cell) shown by (+) etc., the polymer battery using the conductive polymer, etc.

[0051] by the way, the above (1) formula -- or -- the feature which the low-molecular-weight organic silicon compound expressed with (2) formulas mentioned above -- in addition, while being essentially hypoviscosity, the viscosity change in the temperature requirement of a cell busy condition is small, and it has the feature which stability says further that it is high and there is little chemical change by the cell voltage That is, a low-molecular-weight organic silicon compound is stable also in about [ which is the high field of the oxidation reduction potential of the usual nonaqueous-solution system cell ] 5V, and change which has a bad influence on a cell reaction is not shown, but acts on the front face of an electrode active material further, and gives a desirable surface treatment.

[0052] Therefore, as the operation form of the manufacture method of this invention mentioned above described, even if the low-molecular-weight organic silicon compound used for dissolution extraction of a plasticizer remains, it cannot have a bad influence on a cell property, and a low-molecular-weight organic silicon compound can be used as one component of the nonaqueous-solution system electrolytic solution still more positively. The nonaqueous-solution system electrolytic solution for cells of this invention consists of a nonaqueous-solution system electrolytic-solution constituent which contains a low-molecular-weight organic silicon compound inevitably or positively as described above.

[0053] A low-molecular-weight organic silicon compound is the hypoviscosity, and viscosity change can make the nonaqueous-solution system electrolytic solution contain it as an ion conductivity improver using the property of being small. Since the volatility of metal ions, such as a lithium ion, can be raised and the good ion conductivity can be kept stable by this, it becomes possible to obtain a cell with little temperature dependence.

[0054] Since the low-molecular-weight organic silicon compound as this ion conductivity improver

not only contributes to the viscosity down of the nonaqueous-solution system electrolytic solution, but has further the operation which raises the surface activity of an electrode active material as described above, it contributes also to improvement in the plain-gauze fibers for plastering of the intercalation of the metal ion in the positive-electrode layer 3 and the negative-electrode layer 6, and a day intercalation. The internal impedance of a cell can be reduced and this enables it to aim at an improvement of cell efficiency.

[0055] Furthermore, as mentioned above, it excels in stability, and a low-molecular-weight organic silicon compound has little chemical change by the cell voltage, and since it is rich in degradation-proof nature, even if it uses it for a long period of time, it can obtain a quality cell with little property degradation by using the nonaqueous-solution system electrolytic solution using the low-molecular-weight organic silicon compound as one component.

[0056] Here, the non-drainage system solvent in the nonaqueous-solution system electrolytic solution is usually used as a mixed solvent which combined the solvent which has a high dielectric constant as mentioned above, and the solvent of hypoviscosity. A low-molecular-weight organic silicon compound can be blended and used for the conventional nonaqueous-solution system electrolytic solution as an ion conductivity improver, as mentioned above, and although used as some low viscosity solvents described above in this case, it is also possible to use as a subject of a low viscosity solvent further. Also in this case, a low-molecular-weight organic silicon compound cannot be overemphasized by functioning as an ion conductivity improver.

[0057] Also in any of a use form of a low-molecular-weight organic silicon compound which was described above, it is desirable to use what is excellent in a low-molecular-weight organic silicon compound and compatibility for other solvents, and a solvation coefficient (SP value) a low-molecular-weight organic silicon compound specifically Since it is five to about six, a solvation coefficient (SP value) It is desirable to use the hydrocarbon system organic solvent which is four to about 13. This is for compatibility to fall, if the difference of a solvation coefficient (SP value) is not much large, and is the more desirable solvation coefficient (SP value) of a hydrocarbon system organic solvent. It is the range of 5-10. as the solvent which specifically has a high dielectric constant -- gamma-butyrolactone (gamma-BL) etc. -- moreover, a tetrahydrofuran (THF), 2-methyl tetrahydrofuran, etc. are mentioned as a hypoviscosity solvent used together That is, as the nonaqueous-solution system electrolytic solution which blended the low-molecular-weight organic silicon compound, an electrolyte, a low-molecular-weight organic silicon compound, and a solvation coefficient (SP value) It is desirable to use the nonaqueous-solution system electrolytic-solution constituent containing about (five to about [ Preferably ] 10) four to 13 hydrocarbon system organic solvent.

[0058] Loadings of the low-molecular-weight organic silicon compound in the nonaqueous-solution system electrolytic solution 3 - 95 % of the weight Considering as the range is desirable. The loadings of a low-molecular-weight organic silicon compound are 3 % of the weight. The hypoviscosity property of the low-molecular-weight organic silicon compound concerned is it hard to be demonstrated to be the following notably, and, on the other hand, it is 95 % of the weight. Since the dielectric constant of a combination solvent composition system will fully be hard to be maintained if it exceeds, it becomes less not suitable in the quality of the solvent for cells. Especially, when considering as the good solvent for cells of the balance which fully demonstrated these both special feature, they are the loadings of a low-molecular-weight organic silicon compound. 5 - 80 % of the weight Considering as the range is desirable.

[0059] the chain-like organic silicon compound to which the low-molecular-weight organic silicon compound used as one component of the nonaqueous-solution system electrolytic solution is expressed with (1) formula -- and -- Although you may be any of the annular organic silicon compound expressed with (2) formulas, a chain-like organic silicon compound with lower viscosity is used preferably. Moreover, it is 95 - 10 % of the weight about the compounding ratio to the annular organic silicon compound of a chain-like organic silicon compound with viscosity lower when using it as such mixture. Considering as the range is desirable and it is 90 - 50 % of the weight more preferably. It is a range.

[0060] The nonaqueous-solution system electrolytic solution which a low-molecular-weight organic

“silicon compound which was mentioned above contained inevitably, or the nonaqueous-solution system electrolytic solution blended positively is preferably used for the solid-state polyelectrolyte type lithium secondary battery of the operation form mentioned above, for example. The concrete composition of a lithium secondary battery is as having mentioned above, and the lithium secondary battery using the solution system electrolytic solution containing this low-molecular-weight organic silicon compound serves as an operation form of the solid-state polyelectrolyte type cell of this invention.

[0061] Moreover, irrespective of the existence of intervention of a plasticizer, it can be used for the various solid-state polyelectrolyte type cells mentioned above, and also the solution system electrolytic solution containing the above-mentioned low-molecular-weight organic silicon compound can be used as the electrolytic solution of not only a solid-state polyelectrolyte type cell but various kinds of nonaqueous-solution system cells.

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[Translation done.]

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**EXAMPLE**


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[Example] Next, the concrete example of this invention is explained.

[0063] examples 1-2 and the examples 1-4 of comparison -- the example of the manufacture method of the solid-state polyelectrolyte type cell of this invention is explained first It is LiCoO<sub>2</sub> as an active material of a positive electrode. The lithium content cobalt oxide expressed. (Japan Metals & Chemicals Co., Ltd. make), as the high molecular compound which holds acetylene black and the nonaqueous-solution system electrolytic solution as a conductive material, and functions as a binder (VdF-HFrho) -- copolymer powder (the product made from ERUFATOKEMU --) Kynar 2801 and the copolymerization ratio of VdF:HFP prepared the dibutyl phthalate (DBP) as 88:12 and a plasticizer, and in the acetone as a solvent, it mixed and they pasted these so that it might be set to 56:5:17:22 by the weight ratio. About 150 micrometers in thickness it is thin in a positive-electrode layer by vaporizing the above-mentioned solvent after applying this paste by the knife coating machine on the aluminum mesh as a charge collector The plasticizer content stratified Plastic solid was produced.

[0064] The DBF same as the copolymer powder same (VdF-HFrho) as a high molecular compound which holds a mesophase pitch based carbon fiber (Product made from PETOKA) and the nonaqueous-solution system electrolytic solution as an active material of a negative electrode, and functions as a binder on the other hand as a positive electrode, and a plasticizer as a positive electrode was prepared, in the acetone as a solvent, it mixed and these were pasted so that it might be set to 58:17:25 by the weight ratio. Thickness abbreviation which serves as a negative-electrode layer by vaporizing the above-mentioned solvent after applying this paste by the knife coating machine on the copper mesh as a charge collector 130 micrometers The plasticizer content stratified Plastic solid was produced.

[0065] Next, like the above-mentioned positive electrode and the above-mentioned negative electrode, in the acetone as a solvent, it mixed and the copolymer (VdF-HFP) as a high molecular compound and DBP as a plasticizer holding the nonaqueous-solution system electrolytic solution were pasted so that it might be set to 50:50 by the weight ratio. About 90 micrometers in thickness which exfoliates from a glass plate and serves as a base-material layer of a solid-state polyelectrolyte layer after applying this paste by the knife coating machine on a glass plate and vaporizing the above-mentioned solvent The plasticizer content stratified Plastic solid was produced.

[0066] Thus, after carrying out the laminating of the stratified Plastic solid and charge collector used as the stratified Plastic solid used as a charge collector [ used as the obtained positive electrode ] and stratified Plastic-solid, and solid-state polyelectrolyte layer, and a negative electrode in this sequence, it was stuck by pressure by the hot calender roll of 403K, and the laminated-structure object which becomes the origin of the cell cell 8 shown in drawing 1 was produced.

[0067] Next, hexa methyl disiloxane (MM) was first used for the extracting solvent of DBP as an example 1, the above-mentioned laminated-structure object was immersed in MM of ordinary temperature, dissolution extraction was carried out and DBP which is a plasticizer was removed. It is the degree of ultraviolet-rays spectral extinction about the removal grade of DBP. 275 micrometers As a result of pursuing on wavelength, it is time until it is no longer detected. They were 5 - 8 minutes.

[0068] Moreover, octamethylcyclotetrasiloxane (D4) was used for the extracting solvent of DBP as an example 2, the laminated-structure object produced similarly was immersed in D4 of ordinary

temperature, dissolution extraction was carried out and DBP which is a plasticizer was removed. As a result of pursuing the removal grade of DBP like an example 1, it is time until it is no longer detected. It was 7 - 10 minutes.

[0069] As an example of comparison with this invention, diethylether (example 1 of comparison), the methanol (example 2 of comparison), and the laminated-structure object through which it passed and that was produced similarly, using Korean geisha (example 3 of comparison) respectively were immersed in the extracting solvent of DBP at each organic solvent of ordinary temperature, dissolution extraction was carried out and DBP which is a plasticizer was removed. As a result of pursuing the removal grade of DBP like an example 1, time was 10 - 15 minutes, 17 - 25 minutes, and 30 - 40 minutes, respectively until it was no longer detected.

[0070] It turns out that MM of an example 1 and two example D4 are extremely excellent in the extraction capacity of DBP so that clearly from the above-mentioned removal result of DBP. MM and D4 have [ this ] small surface tension compared with the extracting solvent of the example of comparison -- originating -- \*\*\*\* -- the sake -- MM and D4 -- the interior of the laminated-structure object of a cell -- deep -- alike -- until -- it permeates promptly and this can remove DBP in a short time

[0071] Moreover, since an extracting solvent needed vaporizing promptly and not making it remain from a laminated-structure object after extraction of DBP is completed (however, there is nothing a between title even if it remains in the case of low-molecular-weight organic silicon compounds by this invention, such as MM), the cell laminated-structure object concerned was left in the room temperature after the removal end of DBP, and time until an extracting solvent stops remaining inside was measured. Consequently, the example 1 was [ each example of comparison of the example 2 ] 10 - 15 minutes, 50 - 70 minutes, and 120 minutes or more for 17 to 22 minutes for 15 to 20 minutes, respectively.

[0072] Thus, to the cell laminated-structure object of each example which removed DBP completely, and each example of comparison, it is a volume ratio about ethylene carbonate (EC) and dimethyl carbonate (DMC). It is one-mol LiPF<sub>6</sub> at ordinary temperature to the mixed solvent mixed by 2:1. The \*\*\*\*\* system electrolytic solution which dissolved and prepared the electrolyte was sunk in, respectively. this wet out rate is very quick -- also after that, although the amount of saturation sinking in is mostly reached in 5 minutes, in order to sink in, in this example, a few was immersed for 20 minutes and infiltrated

[0073] Thus, obtained area 4cm<sup>2</sup> About the cell cell of each example and each example of comparison, the rate of impregnation, ionic conductivity, and internal impedance of the electrolytic solution were measured. Moreover, about each cell cell into which these electrolytes were infiltrated, after charging to 4.2V by the charging current of 1C, the charge-and-discharge cycle which discharges with the current of 1C to 2.7V was repeated, and each capacity maintenance factor to the initial cell capacity of a deed, the initial cell capacity (mAh) of 1 cycle eye and 10 cycles, 50 cycle, and a 100 cycle eye was measured. These measurement results are shown in Table 1. In addition, except not using DBP in the above-mentioned example, the example 4 of comparison shown in Table 1 produces a cell cell similarly, and performs same measurement about this cell cell.

[0074]

[Table 1]

	DBP 抽出溶媒	電解液 含浸率 (wt%)	イオン 伝導度 (S/cm)	内部 インピーダンス ( $\Omega$ )	初期 容量 (mAh)	容量維持率(%)		
						100回	500回	1000回
実施例1	ヘキサフルオロリン酸トリメチル	65	$4.3 \times 10^{-2}$	57	13	97	92	90
実施例2	オクタフルオロリン酸トリメチル	68	$4.5 \times 10^{-2}$	60	12	98	95	92
比較例1	エチレンカーボネート	58	$8.1 \times 10^{-3}$	139	9	96	93	89
比較例2	メタノール	51	$2.0 \times 10^{-3}$	205	5	91	87	81
比較例3	ヘキサン	53	$2.5 \times 10^{-3}$	188	7	92	85	77



Since hexa methyl disiloxane (MM) and octamethylcyclotetrasiloxane (D4) do not shrink a high molecular compound, in an example 1 and the example 2, they can enlarge rate of impregnation of the electrolytic solution, and, therefore, are understood that ionic conductivity is good, initial cell capacity is large and a charge-and-discharge cycle property is also good, so that clearly from Table 1. Moreover, based on the reforming effect on the front face of an active material by MM or D4, for this reason, the thing with the low internal impedance of a cell can fully supply cell capacity to a load, and is excellent in the so-called cell efficiency.

[0075] In order to shrink the high molecular compound concerned at the same time it extracts DBP from a high molecular compound to these by each extracting solvent by the examples 1-3 of comparison, the amount of sinking in of the part ion electrolytic solution decreases, the initial cell capacity of a cell is low, and a charge-and-discharge cycle property is also bad. Moreover, the internal impedance of a cell is also known by that it is high compared with an example.

[0076] In addition, the result with the same said of the case where replaced with MM of the above-mentioned example 1, and octamethyl trisiloxane (MDM) and a decamethyl tetrapod siloxane (MD2M) are used was obtained, and the result with the same said of the case where replaced with the two above-mentioned example D4, and decamethyl cyclopentasiloxane (D5) is used was obtained.

[0077] Examples 3-4, the example 5 of comparison, next the example of the solid-state polyelectrolyte type cell of this invention are explained.

[0078] The mixed weight ratio of this, methylethyl carbonate (MEC), and gamma-butyrolactone, using hexa methyl disiloxane (MM) as a low-molecular-weight organic silicon compound About the partially aromatic solvent (solvation coefficient (SP value) =9.5) of 1:1, the compounding ratio of MM is 30 % of the weight to the above-mentioned partially aromatic solvent. It mixes so that it may become, and it is in ordinary temperature to this mixed solvent. One-mol LiPF<sub>6</sub> The electrolyte was dissolved and the nonaqueous-solution system electrolytic solution (example 3) was prepared.

[0079] Moreover, octamethylcyclotetrasiloxane (D4) is used as a low-molecular-weight organic silicon compound, and, for the weight ratio of this, dimethyl carbonate, and a sulfolane, the compounding ratio of D4 is 45 % of the weight about the liquid (solvation coefficient (SP value) =10.2) of 2:1. It mixes so that it may become, and it is in ordinary temperature to this mixed solvent. Two mols LiBF<sub>4</sub> The electrolyte was dissolved and the nonaqueous-solution system electrolytic solution (example 4) was prepared.

[0080] Furthermore, it is a weight ratio about methylethyl carbonate (MEC) and gamma-butyrolactone as an example 5 of comparison. It mixes so that it may be set to 1:1, and it is in ordinary temperature to this mixed solvent. One mol LiPF<sub>6</sub> The electrolyte was dissolved and the nonaqueous-solution system electrolytic solution was prepared.

[0081] It sank into the cell laminated-structure object which produced each nonaqueous-solution system electrolytic solution by each examples 3 and 4 and the example 5 of comparison which were mentioned above like the above-mentioned examples 1 and 2 and the example 1 of comparison, respectively (sinking-in time =20 minute).

[0082] Thus, obtained area 4cm<sup>2</sup> About the cell cell of each example and each example of comparison, the rate of impregnation, ionic conductivity, and internal impedance of the electrolytic solution were measured. Moreover, about each cell cell into which these electrolytes were infiltrated, after charging to 4.2V by the charging current of 1C, the charge-and-discharge cycle which discharges with the current of 1C to 2.7V was repeated, and each capacity maintenance factor to the initial cell capacity of a deed, the initial cell capacity (mAh) of 1 cycle eye and 10 cycles, 50 cycle, and a 100 cycle eye was measured. These measurement results are shown in Table 2.

[Table 2]

	電解液 含浸率 (wt%)	イオン 伝導度 (S/cm)	内部 インピーダンス ( $\Omega$ )	初期 容量 (mAh)	容量維持率(%)		
					10回	50回	100回
実施例 3	70	$1.5 \times 10^{-2}$	61	12	97	95	90
実施例 4	67	$9.6 \times 10^{-1}$	45	14	99	96	92
比較例 5	63	$5.0 \times 10^{-3}$	165	9	97	94	82

It turns out that the cell using the nonaqueous-solution system electrolytic solution which blended hexa methyl disiloxane (MM) and octamethylcyclotetrasiloxane (D4) is excellent in each of ionic conductivity, internal impedance, initial cell capacity, and charge-and-discharge cycle properties so that clearly from Table 2. Especially, in the example 3 and the example 4, since ionic conductivity improved by leaps and bounds, even if it performed the charge and discharge of 2-3C, the flattery nature of movement between poles of electrolyte ion was good, and, thereby, broadening was shown in the correspondence to the big load of boosting charge and service capacity.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the perspective diagram showing the important section composition of the solid-state polyelectrolyte type lithium secondary battery by 1 operation gestalt of this invention.

[Description of Notations]

- 1 .... Positive electrode
- 2 5 .... Charge collector
- 3 .... Positive-electrode layer
- 4 .... Negative electrode
- 6 .... Negative-electrode layer
- 7 .... Solid-state polyelectrolyte layer
- 8 .... Cell cell

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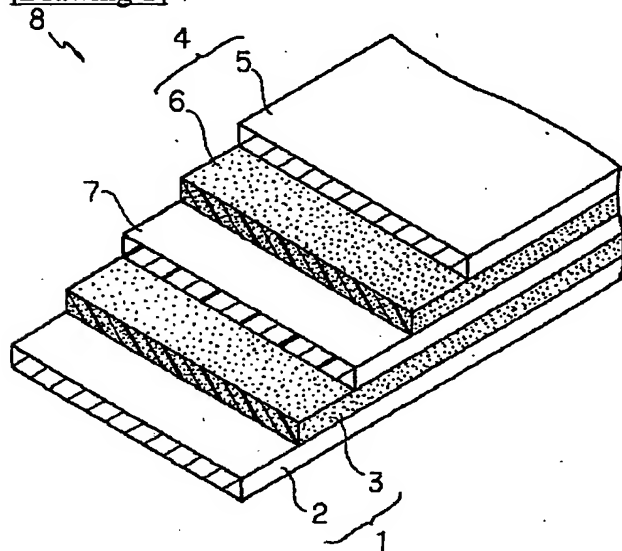
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DRAWINGS

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[Drawing 1]



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